International Journal of Engineering & Scientific Research
Vol. 5 Issue 2, February 2017,
ISSN: 2347-6532 Impact Factor: 5.900
Journal Homepage: http://www.esrjournal.com Email: esrjeditor@gmail.com
Double-Blind Peer Reviewed Refereed Open Access International Journal - Included in the International Serial Directories Indexed & Listed at: Ulrich's Periodicals Directory ©, U.S.A., Open J-Gage as well as in Cabell's Directories of Publishing Opportunities, U.S.A

A sustainable method for the removal of Nickel from aqueous solution using a green material

* Dr Abha Dubey, Dr Seema Kohli, Dr Shalu Tyagi
Associate Professor Department of Chemistry,
MMH College, Ghaziabad, 201009, India

Abstract

The presence of high levels of heavy metals in industrial waste water has assumed a dangerous proportion of pollution of water resources. Among others, nickel is very commonly seen in different concentration ranges in the industrial runoff. It has a potential to affect the entire ecosystem severely if not treated properly. Green technologies have been used frequently for purification of water contaminated with heavy metal ions. Biosorption is a reasonably efficient technique of water purification which is cost effective and eco-friendly too. The present study is about using locally available Portulacaoleracea plant biomass without any chemical treatment for nickel removal from aqueous solution. Batch experiments were performed at room temperature. The effects like change in pH, shaking speed, contact time, metal ion concentrations and biosorbent doses on removal of nickel ions were the critical parameters studied. The optimum conditions of biosorption were observed and evaluated. The maximum removal was found to be 78 % andbiosorption seen increasing with change in pH for a range 2 to 6. The process complied well with pseudo-second order kinetic model. The equilibrium adsorption results closely followed the Langmuirisotherms. The biomass used in the present study found to be a potential green material for removal of nickel from aqueous solution.

KEY WORDS Biosorption, Isotherms, Plant biomass, pseudo second-order

INTRODUCTION

Due to unrestrained and unregulated discharge of industrial effluents in water bodies the level of contaminants significantly polluted in aquatic ecosystems increasing the toxicity of water streams (Akhtar et al., 2013).Heavy metals are the major environmental problem with a global concern. Heavy metals do cause undiminished toxicity and are found to have detrimental effects on the living health systems; hence their removal is seen as of utmost importance and concern. Nickel is one of the non-biodegradable toxic heavy metals present in wastewater. Ni(II) is an essential nutrient needed by the body in trace amounts because it takes part in the synthesis of vitamin B12 and is identified as a component in a number of enzymes, participating in important metabolic reactions, such as ureolysis, hydrogen metabolism, methane biogenesis, and acidogenesis, but Ni(II) ion intake beyond permissible limits results in different types of disease such aspulmonary fibrosis, renal edema, skin dermatitis, and gastrointestinal distress (*e.g.*, nausea, vomiting, diarrhea) (Wuana&Okieimen 2011). Exposure to nickel may cause cancer of lungs, nose and bones. Moreover, it may cause extreme weakness, dermatitis, headache, dizziness and respiratory distress (Kasprzak et al. 2003).

Toxicity of nickel causes pulmonary fibrosis and inhibits many enzymatic functions and skin contact with nickel causes a painful, fatal disease called “nickel itch”. The higher concentration of nickel causes harmful health effects like headache, dizziness, nausea, dry cough, tightness of the chest, chest pain, vomiting, and shortness of breath, nasopharynx, cyanosis, extreme weakness, renal edema, skin dermatitis, gastrointestinal disorder and rapid respiration (Roy & Bhattacharya 2015). The permissible limit of nickel in industrial wastewaters is 2.0 mg/L by WHO guidelines, and the concentration of Ni (II) in industrial wastewaters ranges from 3.40 to 900 mg/L (MINAS Pollution Control Act, 2001). According to the US Environmental Protection Agency (EPA), the maximum the acceptable nickel range for life time is 0.1 mg/L (EPA 2002). The permissible limit of nickel in drinking water given by U.S. Environmental Protection Agency (EPA) is 0.015 mg/l.

Nickel is generally present in the effluents of industrial production processes such as mining, painting, steam electric power generation, galvanization, smelting, dye manufacturing, battery manufacturing and metal finishing (Al-Qodah 2006). Most common sources of nickel to the environment are combustion of coal, diesel oil and fuel oil, the incineration of waste and sludge, use of phosphate fertilizers, stainless steel industry, galvanization, smelting, dyeing operation, batteries manufacturing, metal finishing, jewellery manufacturing, coinage, catalyst, nickel mining and processing etc. Industrial emissions add more than 100 times more nickel than that from natural sources e.g. in effluents of electroplating industries to the tune of 20-200 ppm. Therefore, it is of prime importance to get Ni (II) removed from industrial wastewaters before discharging them into the environment. Conventional methods include coagulation, adsorption, chemical separation, filtration, membrane separation, ion exchange, aerobic and anaerobic treatment advanced oxidation process, electrolysis, microbial reduction, solvent extraction, electrochemical treatment, electro floatation, froth floatation, reduction, chemical precipitation, ion exchange, reverse osmosis, dialysis, activated sludge and adsorption by coated carbon. Most of these methods are generally expensive and so are not affordable for developing countries. These methods are associated with disadvantages such as use of toxic reagents, incomplete removal of heavy metals, high energy requirements, generation of toxic wastes, non-selective, costlier due to operation, maintenance and produces sludge or secondary pollutants which also require proper disposal . There is a need for safe and economical methods for the removal of heavy metal ions from polluted water, so adsorption process is one of the easier, safer and rather cost-effective processes for heavy metal removal from industrial effluents. This has therefore led to the use of adsorbents which have been found significant popularity because of their lower production costs, abundance of those ingredients in nature, low cost of their regeneration and further that they can be simply discharged after expiration. A number of technologies are available with varying degrees of success to control water pollution, such as coagulation, froth flotation, filtration, ion exchange, aerobic and anaerobic treatment, advanced oxidation processes, solvent extraction, adsorption, electrolysis, microbial reduction and activated sludge (Raval et al. 2016). However, most of them require multi-step processing and their use is restricted because of limited removal efficiency, sensitive operating conditions and cost factor.

Metal biosorption on to plant based materials is a complex process affected by several factors. Mechanisms of biosorption include chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, micro-precipitation, heavy metal hydroxide condensation on the biosurface, and surface adsorption. Physisorption is a reversible phenomenon resulting from intermolecular forces of attraction (e.g. weak Vander Waals forces of attraction) between molecules of the biosorbent and the adsorbate. It takes place with formation of multi layers of adsorbate on adsorbent. Chemisorption or chemical adsorption is an irreversible phenomenon and is also called as activated adsorption (Yadla et al., 2012). It occurs as a result of the chemical interaction or chemical forces of attraction or chemical bond between the solid and the adsorbed substance. It takes place with formation of uni-layer of adsorbate on adsorbent. Biosorption process is considered as a desirable method because of its convenience, easy handling, lower operating costs and high efficiency in removing heavy metals from dilute solutions even at low concentrations.

Biosorption is effectively used at low concentrations range (below 100 mg/l) where other technologies are ineffective or costlier. Biomass used for biosorption may be living or dead, while the use of dead biomass or derived products may be easier to use. Heavy metals can be removed by agro-industrial waste products due to their low cost and bulk availability. Recently, potential biosorbent such as non-living biomass of plant wood, saw dust (Rehman et.al 2006) roots, leaves, bark (Vinod et al. 2010) grape stalk waste have been used for the treatment of aqueous solutions of Ni(II).The active surface groups present in the biosorbent work better than mono functional ion exchangers. Plant materials displayed good adsorption capacities and some of them were comparable with commercially available activated carbons and synthetic resins. Biosorption can be used as economical and eco-friendly technology in comparison to other technologies used for heavy metal removal.

In our earlier studies we have used PPBM for the removal of lead, cadmium and chromium. *Portulaca* is a herbaceous weed can be found growing wild and cultivated in much of the world. *Portulaca* grows in almost any un-shaded area. Phyto-chemical screening of plant showed the presences of many biologically active compounds such as amino acids, alkaloids, carbohydrates, fixed oils, flavonoids, glycoside, phenolic compounds, proteins, saponins, steroids, and tannins. Due to the presence of many functional groups, this plant is found be used as good biosorbent and especially for the heavy metal ions from aqueous solutions.

The present study evaluates the use of Portulacaoleracea plant biomass (PPBM) as a low cost eco-friendly biosorbent with natural chemical composition for removal of Ni (II) ions from dilute aqueous solution. The novelty of this work is the use of simple and environment friendly method for the preparation of biosorbent without any chemical treatment. Batch experiments were conducted to evaluate the effects of different parameters such as pH, contact time, metal ion concentration, temperature and dose of biosorbent on Ni (II) ion removal. Experimental data were applied to different kinetic isotherm and thermodynamic models.

MATERIALS AND METHODS

All chemicals of analytical reagent grade procured from the standard source were used for different batch experiments. De-ionized water was used in all the experiments.

Preparation of green Biosorbent

Plant waste was collected from the local gardens; the collected material (stem and leaves) was washed thoroughly with water to remove dirt and finally washed with de-ionized water. Material was dried in sun for 10 days, and finally in microwave for about 30 minutes in a LG make domestic microwave oven having temperature range 40^0C to 100^0C (Magnetrons are set at a frequency of 2450 M hz) (LG microwave appliance model no. MS-285SD; Korea) at 70^0C. The dried plant material was then ground and sieved. Powdered material of *Portulaca*plant biomass (PPBM) was kept in air tight containers and used as such without any further chemical treatment.

Preparation of Nickel (II) solution

Stock solution was prepared by dissolving 1000 mg/L was prepared by dissolving nickel nitrate [Ni $(NO_3)_2 \cdot 6H_2O$] in one litre of de-ionized water. Initial pH values of the solution was adjusted in the range 3-7 for different experiments by adding 1N HCl /1N NaOH. The stock solution was diluted and used for different concentrations required for the experiments.

Batch experiments

All experiments wereperformed in 250 ml Erlenmeyer flasks on thermo stated orbital shaker. Test solutions of different concentrations (10-250 mg/L) were prepared by diluting the stock solution. Different amount of PPBM (0.25-1.5 gm) was added to different test solutions for different batch experiments. Volume of the test solution was 200 ml. The effect of different parameters such as pH, shaking speed, contact time, initial metal ion concentration, and dose of PPBM were tested by varying only one of the parameters at a time while others remain fixed.

The samples were taken out from the test solution after definite time intervals till the equilibrium was reached. The biosorbent was separated by filtration with whatman filter paper number 41 followed by centrifugation at 3000 rpm for 10 minutes. The concentration of Ni (II) in the filtrate was analyzed using an Atomic Adsorption Spectrophotometer (GBC Avanta). Data obtained were used for different studies. Blank samples were also run under similar conditions. All the experiments were conducted in triplicates and the mean value (values ranges within ±2) was used in the calculations.

RESULTS AND DISCUSSION

Effect of pH

The biosorption of metal ions from aqueous solution depends on the pH of the solution since it affects surface charge, degree of ionization of the functional groups, and metal ion speciation (Flaviane et al., 2010). Solubility of metal ions, concentration of counter ions on the functional groups of the biosorbent and the degree of ionization of the adsorbate is mostly affected by the pH of the solution. The experiments were carried out by adding 1g of PPBM in 200 ml solution of 200 mg/L of nickel (II) concentration at pH values from 3 to 7. The acidic range of PH was chosen because the industrial wastewaters are often acidic and heavy metals stats precipitating in the basic medium. Removal increases with increasing pH from 3-7 maximum removal of 78.4 % was at pH 6, results are shown in figure 1. At lower pH values removal of nickel was less, possibly due to the competition between hydrogen and nickel ions on the sorption site. With an apparent dominance of hydrogen ions in the solution at low pH, these ions seem to restrict due to the repulsive force (Yipmantin et al. 2011). Biosorption of nickel ions was maximum at pH 6 so this was taken as an optimum pH and used in all other experiments.

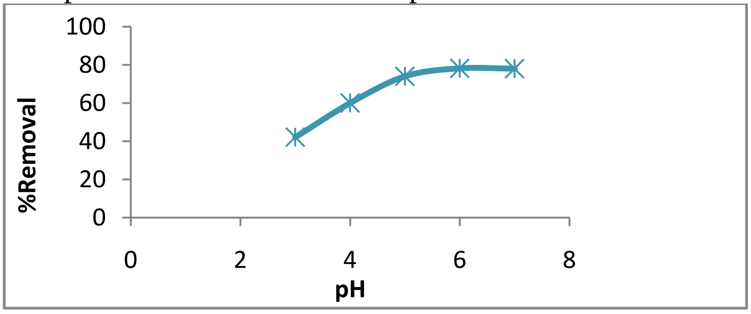

Figure: 1 Effect of pH

Effect of shaking speed

Experiments were done by varying shaking speed (50-300 rpm), using 1 gm PPBM, and Ni (II) ion concentration as 200 mg/L at pH 6. The effect of shaking speed is shown in Fig.2. Removal increases with increase in shaking speed initially and remain constant after 250 rpm speed, at 250 rpm and maximum removal was 78%. This speed was considered as optimum speed and maintained for all other experiments. Low biosorption at low shaking speed may be due to lack of affinity of adsorbent with the nickel ions present in the solution. Increases in removal with the increased shaking speed may be explained by its influence on the distribution of the solute in the bulk solution and the formation of external boundary film. High speed reduces the boundary-layer resistance and increases the mobility of the system (Kyzas, 2012).

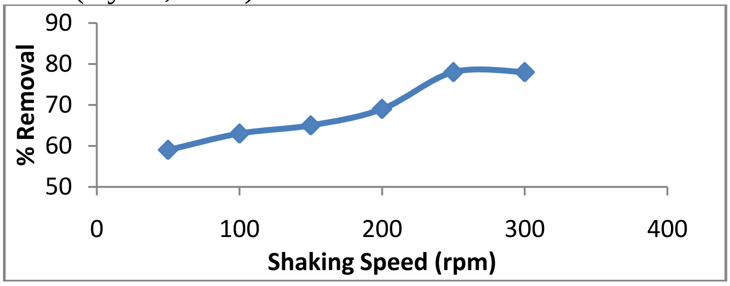

Figure: 2 Effect of shaking speed

Effect of contact time & metal ion concentration

Different experiments were conducted using different metal ion concentration from 10-200 mg/L, contact time ranged from 15-75 minute, PPBM dose was fixed as 1 gm at pH 6. Results are shown in Fig. 3; which clearly shows that for all the different concentration of nickel (II) removal increases with increase in contact time, and become constant after some time. Equilibrium was achieved in 60 minutes maximum removal was again 78.4% as shown in Figure 3. Removal was very fast initially it may be due to the fact that for biosorption the large number of vacant sites was available, later due to exhaustion of remaining surface sites and repulsive force between solute molecule and bulk phase (Saravanane et al. 2002) removal becomes slow. Equilibrium time was independent of initial Ni (II) ion concentration as shown in the results. Removal was maximum at the 200 mg/L concentration of nickel (II) ions in the solution. For further experiments this was used as the optimum dose.

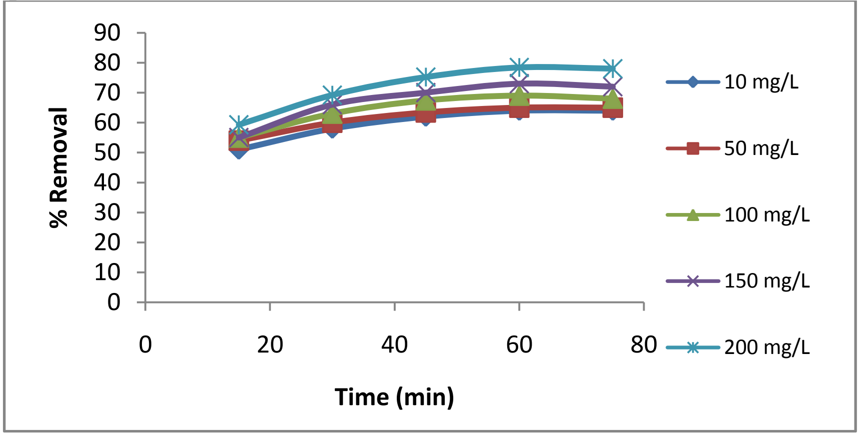

Figure: 3 Effect of contact time & metal ion concentration

Effect of biosorbent dose

The dependence of Ni (II) biosorption on PPBM dose was studied by varying the amount from 0.25 to 1.5 g while keeping the volume 200 ml and concentration of nickel ion 200 mg/L, pH 6 and contact time 60 min. The removal of nickel increased from 59.2 to 78.4% with an increase in PPBM dose (Fig. 4) and finally attains a steady value. Hence, 1 g/L PPBM was taken as the optimum dose.An increase in removal percentage with an increase in biosorbent dose may be attributed to the availability of more sorption sites present on the surface of the biosorbent (Thirumavalavan et al. 2011).

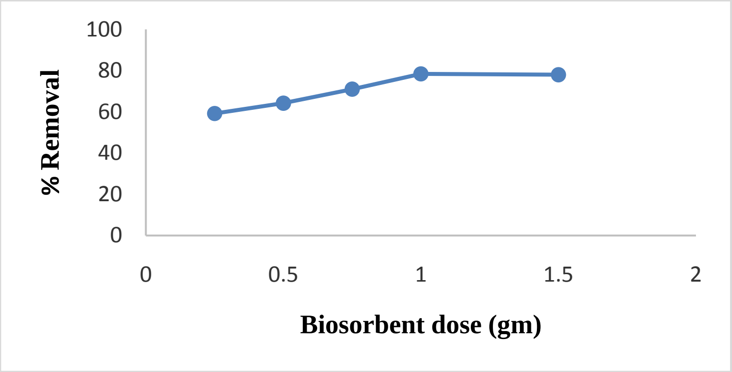

Figure: 4 Effect of Biosorbent dose

Biosorption Kinetic studies

The kinetics of metal biosorption governs the rate, which determines the residence time and is one of the important characteristics defining the efficiency of biosorbent.For designing an appropriate biosorption system kinetics is the main factor to study. The biosorption kinetics can be controlled by several independent processes which could act in series or in parallel, such as external mass transfer, bulk diffusion, chemisorptions and intra particle diffusion. Two models, pseudo-first order (Lagergren, 1898) and pseudo- second order (Ho and Macky, 1999) were applied for the study.Lagergren pseudo first-order model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites i.e. rate of change of solute uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time. The general form of this model is expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (1)$$

q_e and q_t are amount of metal ion (mg/g) at time t and at equilibrium respectively. k_1 is the rate constant of pseudo first-order adsorption. Integrated form of equation is

$$\frac{q_t}{q_e} = 1 - e^{(-k_1 t)} \qquad \textbf{Or} \qquad \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (2)$$

The pseudo-second-order kinetic expression was developed by (Lagergran and Venska1898) to describe the biosorption of metal ions. The pseudo second order model (Ho and McKay, 1999)is based on sorption capacity of solid phase.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (3)$$

Where k_2 is rate constant of pseudo second-order adsorption (g mg^{-1}min^{-1}). Integrated linear form of equation is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

The applicability of the above two models were examined by each linear plot of *ln*(qe-q) vs. t, and (t/q_t) *vs.* t, respectively. The validity of the kinetic models is tested by the magnitude of the regression coefficient R^2.

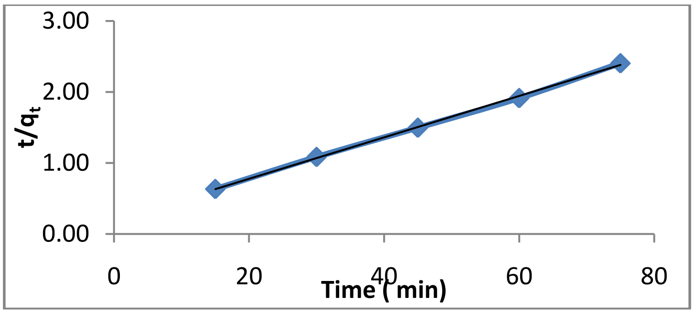

Figure: 5 Pseudo second order kinetics plot

The high regression value 0.999 explains that the process favours the pseudo second-order model in comparison to pseudo first-order.

Isotherms studies

Adsorption isotherm is very useful in giving information about adsorption mechanisms, surface properties and affinity of an adsorbent towards heavy metals ions. These isotherms are generally used to establish the relationship between the amount of metal ion biosorbed and its equilibrium concentration in solution. They also help to provide vital information to understand the mechanism of the adsorption process. (Ncibi2008) A number of isotherms have been developed to describe equilibrium relationships. In this study, the Langmuir, Freundlich isotherm models were used.

The Langmuir model (Langmuir 1916) is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by

$$\frac{1}{Q_e} = \frac{1}{qbC_e} + \frac{1}{q} \qquad (5)$$

Q_e = Ni (II) ions concentration at equilibrium (mg /g),
q = maximum metal uptake per unit mass of PPBM (mg/g) adsorption capacity
b = Langmuir constant (L) related to energy of sorption
C_e = Concentration of Ni (II) ions in aqueous phase

Here b reflects quantitatively the affinity between the PPBM and Ni (II) ions. The values of q and *b* are the characteristics of the Langmuir model. They can be determined by linearizing above equation.

$$\frac{C_e}{Q_e} = \frac{1}{qb} + \frac{1}{qC_e} \qquad (6)$$

A plot of 1/Qe versus $1/C_e$; gives a straight line of slope 1/qb and intercept 1/ (*q*). The value of Q_e was calculated from the following equation:

$$Q_e = (C_i - C_e)/(m/v) \qquad \textbf{(7)}$$

C_i = initial concentration of Ni (II) ions in the solution (mg/L)
C_e = concentration of Ni (II) ions at equilibrium
v = initial volume of Ni (II) ions solution used (L)
m = mass of PPBM used (g)

The essential features of Langmuir isotherm can be used to predict the affinity between biosorbent and metal ions this is expressed in terms of dimensionless constant called separation factor or equilibrium parameter R_L, predicts whether an adsorption system is favourable or unfavourable. R_L is defined by following equation.

$R_L = 1/(1+b\,C_0)$ (8)

Where b is Langmuir constant and C_0 is initial concentration of Ni (II) ion. Value of R_L indicates the isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$), unfavourable if ($R_L > 1$).

The Freundlich isotherm model (Freundlich 1906) is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of nickel (II) adsorbed per unit mass of adsorbent, *qe*, and the concentration of the nickel at equilibrium, *Ce*.

Freundlich isotherm: $Q_e = KC_e^{1/n}$ (9)

K= Freundlich constant indicating the adsorption capacity

n= Freundlich constant, indicating the adsorption intensity

The above equation is rearranged in linear form to give:

$\log Q_e = \log K + 1/n \log C_e$ (10)

Freundlich constants K and n, were calculated from the intercept and slope of the plot of log Qe versus log *C*e .

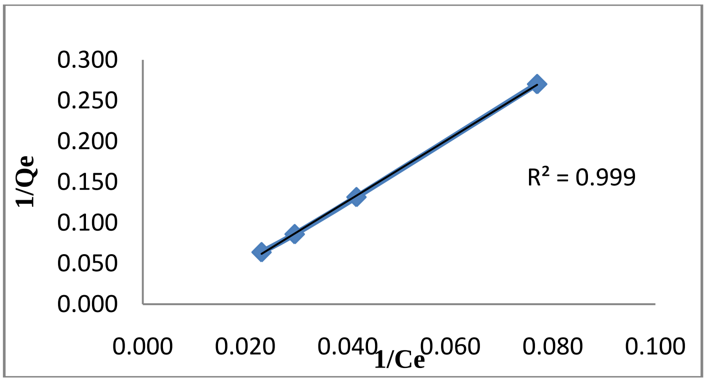

Figure: 6 Langmuir isotherm model

Fig. 6 shows that, the Langmuir model yields a much better fit than the Freundlich model, as the correlation coefficient (R^2) value is higher. Value of q was calculated as 76.923 mg/g and R_L was found to be 0.426 from this value it is confirmed that PPBM is a favourable biosorbent for nickel ions.

CONCLUSION

Portulacaplant biomass(PPBM) biomass was selected for studying biosorption due to the possibility of utilizing a waste biomass to eradicate the metal pollution. Optimum pH was found to be 6. Langmuir isotherm was the best fitted model with adsorption capacity of 76.923 mg/g. Pseudo-second order was best fitted kinetic model. The outcome of this study shall help in designing the biosorbent used in the industry for removal of Ni (II) ions from their effluents. Moreover, the use of PPBM shall minimize the use of activated carbons, which are usually obtained from wood, thus protecting our environment.

REFERENCES

1. Akhtar, M.S., Chali B. and Azam, T.(2013).Bioremediation of Arsenic and Lead by Plants and Microbes from Contaminated Soil.Res. Plant Sci., 1(3) : 68-73.
2. Al-Qodah Z (2006) Biosorption of heavy metal ions from aqueous solutions by activated sludge. Desalination 196:164–176

3. EPA U (2002) Edition of the Drinking Water Standards and Health Advisories US Environmental Protection Agency Washington^ eDC

4. Freundlich HMF (1906) Over the adsorption in solution. J PhysChem 57:385–471
5. Flaviane VK Leandro VA, Laurent GF (2010). Removal of Zn from aqueous single metal solutions and electroplating wastewater with wood sawdust and sugar cane bagasse modified with EDTA dianhydride(EDTAD). J. Hazard. Mater. 176: 856-863.

6. Kasprzak, K.S., SundermanJr, F.W. and Salnikow, K. (2003) Nickel Carcinogenesis. Mutation Research: Fundamental and Molecular Mechanisms, 533, 67-97.

7. Kyzas,G.Z,.(2012). Commercial Coffee Wastes as Materials for Adsorption of Heavy Metals from Aqueous Solutions.Materials. 5, 1826-1840.

8. Lagergran SK, Venska S (1898) About the theory of so-called adsorption of soluble substances. VetenskapsakadHandl 24(2):1–39
9. Langmuir I (1916) The constitution and fundamental properties of solids and liquids. J Am ChemSoc 38(11):2221–2295

10. MINAS pollution control acts (2001) Rules, notification issued there under Central Pollution Control Board, Ministry of Environment and Forests Government of India, New Delhi, September

11. Ncibi MC (2008) Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis J Hazard Mater 153:207–212

12. Raval N, Shah P, Shah N (2016) Adsorptive removal of nickel (II) ions from aqueous environment; A review. J Environ Manag 179:1–20
13. Rehman, H., Shakirullah, M., Ahmad, I., Shah, S. and Hameedullah, H. (2006) Sorption studies of Nickel ions on to saw dust of Dalbergiasissoo Journal of the Chinese chemical Society Vol. 53, no. 5, pp. 1045-1052
14. Roy, J. Bhattacharya, Nanotechnology in industrial wastewater treatment. IWA Publishing, 2015, page 14.

15. Saravanane R, Sundararajan T, Sivamurthyreddy S (2002) Efficiency of chemically modified low cost adsorbents for the removal of heavy metals from wastewater: a comparative study”, Indian. J EnvHlth 44:78–81

16. Thirumavalavan M, Lai Y, Lee J (2011) Fourier transform infrared spectroscopic analysis of fruit peels before and after the adsorption of heavy metal ions from aqueous solution. J ChemEng Data 56:2249–2255

17. Vinod VTP, Sashidhar RB, Sreedhar B (2010) Biosorption of nickel and total chromium from aqueous solution by gum kondagogu (Cochlospermumgossypium): a carbohydrate biopolymer. J Hazard Mater 178:851–860

18. Wuana R.A., Okieimen F.E., Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation *Int. Sch. Res. Net.*, (2011) 1-20.

19. Yadla, S. V., Sridevi, V., and Lakshmi, M. V. V. C. (2012). “A review on adsorption of heavy metals from aqueous solution” J. Chem., BiolPhys Sci., 2(3), 1585–1593

20. Yipmantin A, Maldonado H, Ly M, Taulemesse J, Guibal E (2011) Pb(II) and Cd(II) biosorption on Chondracanthuschamissoi (a red alga). J Hazard Mater 185:922–929