Utilization of mesquite (Prosopis juliflora) wood biochar for adsorption of nickel ions in aqueous solution

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Abstract
In this adsorption study, removal of nickel from aqueous solutions has been inquired by mesquite (Prosopis juliflora) wood biochar as a low cost adsorbent. The rate of nickel adsorbed significantly increased with increase in initial concentration of nickel solution and adsorption rate gradually decreased as the dosage of biochar increased at the pH 6 and pH 7. The maximum adsorption rate was obtained 3.05 mg g\(^{-1}\) at the pH 7 with the lower adsorption dosage (0.25\%) of biochar at 20 mg L\(^{-1}\). The percent removal decreased with increased initial concentration of nickel and the percent removal increased with increased dosage of biochar at pH 6 and 7. The maximum percent removal was obtained 91.72\% at the pH 7 at 1.0\% biochar. Also, it helps in reduction of waste generation. Thus, the use of low cost adsorbents may contribute to the sustainability of the surrounding environment.

Keywords: Agricultural waste, Biochar, Heavy metal, Adsorption

Introduction
Heavy metal pollution is mostly spread in to the environment due to rapid industrialization and global urbanization (Kamari et al., 2014)\(^{[1]}\). Heavy metals are non-biodegradable, bio accumulate and highly toxic in terrestrial and aquatic living organisms (Ghani et al., 2013 and Yuvaraja et al., 2014)\(^{[4, 22]}\). Nickel is one crucial heavy metal entering water sources through industrial activities like electroplating, batteries and metallurgical industries (Wantala et al., 2014)\(^{[20]}\). The concentration of nickel in Coimbatore sewers ranging from 9.0-16 mg L\(^{-1}\) (Pavitharapriya et al., 2015)\(^{[13]}\). In India is estimated that about 38,254.0 million litres day\(^{-1}\) (MLD) of wastewater is generated in urban centre (Kaur et al., 2013)\(^{[8]}\). From this 1077.21 MLD of waste water are produced in Tamil Nadu. The alarming health issues of skin allergies due to nickel in wastewaters have increased the need to develop remediation measures to remove metals from water matrices (Ucar et al., 2014)\(^{[19]}\). There are different methods of treatment available to remove heavy metals in wastewater such as adsorption, membrane filtration, chemical precipitation, ion exchange, flocculation, extraction and coagulation (Li et al., 2014 and Tasar et al., 2014)\(^{[10, 17]}\).

Biochar, a pyrolysed carbon rich-porous material from various organic waste materials (Inyang et al., 2016)\(^{[6]}\). Biochar can be used as a low-cost substitute for activated carbon used in the presence of pollutants (Cernansky, 2015)\(^{[2]}\). Furthermore, biochars are considered as a universal sorbents in the removal of organic and inorganic contaminants in both soil and water (Ahmad et al., 2014)\(^{[1]}\). Additionally, biochars with high sorption capacity are considered as suitable feed stocks. If pyrolysed, it opens up a variety of functional groups on surface of then making it suitable to stop variety of contaminants. (Doumer et al., 2016)\(^{[3]}\). In this study, the potential of using Mesquite wood biochar as a low cost biosorbent for removal of nickel in waste water.

2. Materials and Methodology
2.1 Adsorbent
Mesquite (Prosopis juliflora) wood was collected from Paramakudi in Ramanathapuram district. The collected samples were air dried at room temperature for 2-3 days then converted into biochar through pyrolysis at 450\°C. The biochar samples were ground and sieved to 2.0 mm particle size.
Then the Prosopis wood biochar (PWB) was kept in oven at 60°C for 48 hr to reduce the moisture content. After air dried Prosopis wood biochar stored in air tight container for further analysis.

2.2 Adsorbate
Stock solutions of nickel were prepared by dissolving 4.08g of nickel chloride (NiCl₂) in 1000 ml of 1.0% nitric acid solution. 1.0% HNO₃ was used to prevent hydrolysis of metal ions solution. Initial concentrations of metal ions like 5, 10, 15 and 20 mg L⁻¹ were prepared by diluting the 100 mg L⁻¹ of solutions. The pH of the metal solution was adjusted using 1.0M HCl and 1.0M NaOH solutions (Onundi et al., 2010) [12].

2.3 Adsorption characterization of biochar
2.3.1 Scanning Electron Microscope (SEM)
Scanning Electron Microscope (M/s. FEI - Quanta 250, Czech Republic) was used to record the surface texture and morphological characteristics of the biochar samples (Ucar et al., 2014) [19]. The biochar samples were spreaded on double sided conductive carbon tap fixed on the stub. After attaining high vacuum the filament was turned on and adjusted to various required parameters like electron beam, intensity, spot size, voltage, emission current then the SEM images were captured and pore space was measured to study the adsorption properties of biochar.

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)
In this FTIR analysis, biochars were specially used to determine the functional groups present for each temperature and biomass, especially carbons. FT-IR spectra were recorded with 1.0 mg of biochar sample embedded in potassium bromide 30.0 mg (KBr) and then pressed into pellets separately and observed in a FTIR (Model 8400S of Shimadzu, Japan) using Attenuated Total Reflectance (ATR) technique having wavelength source 400-4000 cm⁻¹ (Trakal et al., 2014) [18].

2.4 Batch experiment study
Batch experiments were conducted using varied concentrations (0, 5, 10, 15, 20 mg L⁻¹) of nickel solutions. Different dosage of biochar (0.25, 0.5 and 1.0%) was added to each conical flask. To this 50 ml of nickel at different concentrations of 0, 5, 10, 15, 20 mg L⁻¹ was added and shaken for 8.0 hrs at 250 rpm in mechanical shaker. After sorption, the solution was filtered using Whatman No.42 filter paper. The filtrate was analyzed using Flame Atomic Absorption Spectroscopy (AAS). The amount of heavy metal adsorbed per unit mass of the adsorbent (qₑ) and the percent adsorption of the metal was calculated as follows equation 1 and 2.

\[ qₑ = \left( C_o - C_e \right) \frac{V}{M} \] ................................. (1)
\[ \% = \left\{ \left( C_o - C_e \right) / C_o \right\} \times 100 \] ................................. (2)

Where, \( C_o \) = Initial concentrations of the metal ion in solution (mg L⁻¹), \( C_e \) = Final concentrations of metal ion solution (mg L⁻¹), \( V \) = Solution volume (L) and \( M \) = Mass of the sorbent (g) (Onundi et al., 2010) [2].

3.3. Effect of initial concentration of metal ions
3.3.1 Rate of adsorption of nickel with Prosopis wood biochar at pH 6 and pH 7
The rate of nickel adsorbed significantly increased with increase in initial concentration of nickel solution and adsorption rate gradually decreased as the dosage of biochar increased at the pH 6 and pH 7. The maximum adsorption rate was obtained 3.05 mg g⁻¹ at the pH 7 with the lower adsorption dosage (0.25%) of biochar at 20 mg L⁻¹ (Fig 2). Kavya (2016) [9] reported the rate of nickel adsorption of Coir waste biochar was 3.20 mg g⁻¹ and adsorption rate gradually decreased with an increase the dosage of biochar. This scenario can be explained by the fact that there was a high probability of collision between adsorbent surface and metal ions at high concentrations. Therefore, the rate of diffusion of metal ions towards the adsorbent surface was expected to increase (Kamari et al., 2014) [7].
3.3.2 Percent removal of nickel with *Prosopis* wood biochar at pH 6 and pH 7

The percent removal decreased with increased initial concentration of nickel and the percent removal increased with increased dosage of biochar at pH 6.0 and 7.0. The maximum percent removal was obtained 91.72% at the pH 7.0 in the lower concentration of 5 mg L\(^{-1}\) at 1.0% dosage of biochar (Fig 3). Santuraki and Barminas (2015)\(^{[14]}\) and Kavya (2016)\(^{[9]}\) reported the nickel removal efficiency of coir waste biochar was 82.64% and the percent removal decreased with an increase in the initial metal ion concentration. This was due to low ratio at active sites available on the adsorbent surface to metal ions at high concentration (Yargic *et al.*, 2015)\(^{[21]}\).

3.4 Effect of adsorbent dosage

Adsorbent dosage is other important parameters that should be considered in contriving an effective adsorption system (Tasar *et al.*, 2014)\(^{[17]}\). The amount of adsorbent dosage is directly proportional towards the availability of the active binding sites (Yuvaraja *et al.*, 2014)\(^{[22]}\) and the operational cost. The percentages of nickel removal increased significantly from 15.78 to 62.65% at pH 6.0 and from 28.96 to 91.72% at pH 7.0 for higher concentration to lower concentration of metal solution with the increase of the biochar dosage from 0.25 to 1.0%. The adsorption removal for nickel decreased drastically as the adsorbent dosage increased from 0.25 to 1.0% for increase the higher concentration of metal solutions (Fig 4). A similar observation was reported by Yargic *et al.* (2015)\(^{[21]}\) for metal removal using tomato waste. This phenomenon can be explained by the fact that more active sites are available for metal ion binding at high dosage (Gupta *et al.*, 2013)\(^{[5]}\). An extra amount of adsorbent available also provides high surface area which is favorable for adsorption process (Mahajan and Sud, 2013)\(^{[11]}\).
4. Conclusion
The maximum removal efficiency of nickel by *Prosopis* wood biochar is 91.72 % at 5 mg L\(^{-1}\) at pH 7.0. The rate of sorption of nickel 3.05 mg g\(^{-1}\) increased significantly with increased concentration of nickel in aqueous solution until 20 mg L\(^{-1}\). The adsorption of nickel was increased with increase the concentration of metal solution and biochar dose. The *Prosopis* wood biochar can be used as low cost adsorbent in for nickel removal effectively.

5. References