Potential of Pine Biochar in Removal of Copper from Synthetic Waste Water

Rini Labanya*, P. C. Srivastava and S. P. Pachauri

Department of Soil Science, G.B. pant University of Agriculture & Technology, Pantnagar-263145, Uttarakhand, India

*Corresponding author

Abstract

Mining, industrial processing, smelting and other industrial activities produce waste waters having toxic levels of Cu which have potential to contaminate natural water and soils. The present study focuses on the removal of Cu(II) from synthetic waste water containing Cu levels in the range of 15.9 to 143 mg L\(^{-1}\) onto Pine needle biochars prepared by pyrolysis at 300 (P300) and 450°C (P450). The results indicated that P450 had many fold higher Cu removal capacity which could retain 98% of Cu present in wastewater containing nearly 50 mg Cu/l. The sorption-desorption data of Cu onto P300 and P450 conformed best to Langmuir isotherm as compared to Freundlich adsorption model. Adsorption maxima for Cu sorption of P300 and P450 were 1068.5 and 3516.0 mg kg\(^{-1}\), respectively. The values of constant (k) related to bonding energy P300 and P450 were 0.094 and 0.741 kg mg\(^{-1}\), respectively. Hysteresis index calculated from Freundlich isotherms (n\(_{des.}\)/n\(_{ads.}\)) were 37.3 and 299.5 for P300 and P450, respectively which clearly indicated an irreversible binding of Cu onto pine biochar which might work as a potential cheap adsorbent for remediation of Cu loaded toxic wastewaters.

Keywords
Biochar, Pine, Temperature, Copper, Adsorption, Desorption

Introduction

Heavy metals have been introduced into the environment as a result of industrial production, energy utilization, mining, and the application of pesticides and fertilizers (Ihsanullah et al., 2016; Sankhla et al., 2016; Siddiqui and Pandey, 2019). Copper (Cu II) is a potential toxicant at high doses (Tchounwou et al., 2012). Copper is one of the main waste generated from electroplating industries. According to Environmental Protection Agency (EPA) standards, the tolerance limit of Cu fixed for effluent discharge is 3 mg L\(^{-1}\) (EPA, 1993a). According to the Bureau of Indian Standards (BIS), the desirable concentration limit of Cu in drinking water is 0.05 mg L\(^{-1}\) and in the absence of alternate source the permissible limit is 1.5 mg/L (EPA, 1993b; BIS, 1991). Currently, the treatment strategies for attenuation of heavy metals mainly include chemical precipitation, ionic exchange, reverse osmosis and adsorption. Among these methods, the cheapest and the most effective methods are based on adsorption (sorption) processes occurring on the natural or synthetic adsorbents (Chen et al., 2011; Zhang et al.,...
Among different adsorbents (sorbents), biochars and other carbon adsorbents belong to the most perspective materials (Ahmad et al., 2014; Mohan and Pitmann 2006; Gupta and Nayak 2012; Wang et al., 2018). The widespread use of adsorbents has been limited by the lack of environment friendly and economical adsorbents (Park et al., 2015).

Biochar is a solid material produced during a process known as pyrolysis from the thermo-conversion (slow, intermediate, and fast pyrolysis or gasification) of biomass under little or no oxygen which can also be used in soils as an amendment (Gaskin et al., 2008; Lehmann and Joseph 2009). Biochar can be produced from a range of feedstock, including forest and agriculture residues, such as straw, nut shells, rice hulls, wood chips/pellets, tree bark, bioenergy crops (willows, miscanthus, and switchgrass), forest residues (sawdust, grain crops, and nut shells), organic waste (green yard waste and animal manure), agricultural waste, kitchen waste, and sewage sludge, algae etc. and thus, has varying nutrient contents. The incomplete carbonisation of the biomass during the pyrolysis process changes the properties of the feedstock, resulting in the biochar with a porous structure, high surface area, high pH, active functional groups and a graphite-like aromatic structure (Keiluweit et al., 2010; Manyà 2012; Ronsse et al., 2013; Xin et al., 2015). These properties result in high adsorption capacities of biochar for heavy metals (Keiluweit et al., 2010; Beesley et al., 2011; Inyang et al., 2015). As a complex carbon-rich substance, biochar adsorption mechanism of heavy metals in aqueous solution is very diverse, its surface oxygen-containing functional groups and binding sites can easily make complexation or ion exchange with heavy metal ions; in addition to that, some insoluble inorganic salt (form in the process of preparation of biochar) could co-precipitate with heavy metal ions on the surface. Biochar has been also described as a possible tool for soil fertility improvement, potential toxic element adsorption, and climate change mitigation. Namgay et al., (2010) reported that biochar application decreased the concentration of As, Cd, and Cu in maize shoots, depending on the amount of biochar addition, soil pH, and ability of metal to adsorb on Biochar. Chen et al., (2008) assessed that pine-needle derived biochar was effective in removing nitrobenzene, naphthalene and m-dinitrobenzene from water. Previous studies have also demonstrated that the raw materials substantially affect the physicochemical properties and heavy metal adsorption capacity of biochar; therefore, choosing an appropriate feedstock is critical for the development of an efficient biochar (Suman et al., 2017; Zahedifar, 2017).

The disposal of enormous amounts of fallen pine (Pinus roxburghii) needles, usually found as waste biomass in coniferous forests is a challenge faced by local people as well as natural resource managers. Moreover, it plays a pivotal role in causing devastating forest fire due its high resin content. Extremely slow decomposition rate of pine needle also makes its disposal tough. Therefore, we tested the efficacy of the biochar produced from pine needle to remediate synthetic waste water containing high levels of Cu (II) to reduce heavy metal contamination of soil and water bodies. The specific objectives of this study were to investigate Cu removal capacity of Pine Biochar and to examine adsorption and desorption characteristics of pine biochar for Cu (II).

Materials and Methods

Pine needles were collected from International Guest House of G. B. Pant University of Agriculture and Technology,
Pantnagar, Uttarakhand. These residues were dried to remove the moisture content in the biomass. The dried materials were chopped into small pieces to make them ready for the biochar preparation. Thereafter, these materials were incinerated in the muffle furnace at controlled temperature of 300 and 450°C under limited oxygen supply. The charred materials obtained after the pyrolysis were crushed in pestle and mortal to make them fine and homogenous powder-like material. Crushed samples were passed through 0.5 mm sieve and stored in plastic containers (labeled as PB300 and PB450) for subsequent analysis and use.

Pine biochars (P300 and P450) were analyzed for elemental composition using CHN elemental analyzer. The equilibrium pH and specific electrical conductivity were also determined in 1:10 biochar: water suspensions using pH meter and electrical conductivity meter.

### Adsorption-desorption experiments

Adsorption studies were carried out by equilibrating 0.5 g of biochar (P300 and P450) in duplicate with different concentrations of Cu (II) (0, 2, 4, 6, 8, 10, 12, 14, 16, 18 ml of stock solution containing 0.156 g of CuSO₄·5H₂O in 250 mL in centrifuge tubes. A background solution of 2 mL 0.1 N NaNO₃ was added initially in each tube and the final volume was made up to 20 mL by distilled water. The tubes were then shaken on an orbital shaker at room temperature (25 ± 0.5 °C) at 180 rpm for 48 h. After 48 h, the solid and liquid phases were separated by centrifugation at 8000 rpm for 10 min and then the supernatant was filtered with a 0.45-µm filter and stored in plastic vials for Cu determination by AAS (GBC-Avanta M). The percent removal of Cu (II) was calculated for different initial concentrations of Cu(II).

The amount of Cu (II) adsorbed by pine biochar (q_{ads}) was calculated as:

\[
q_{ads} = \frac{\text{Initial Cu conc. in soln. (mg/L)} - \text{Cu conc. in equil. soln. (mg/L) x Total vol. (mL)}}{\text{Wt. of biochar (g)}}
\]

After adsorption, pine biochar samples subjected to Cu (II) adsorption with the highest Cu (II) concentration were dispersed in 20 mL water containing 2 mL of background electrolyte (0.1 M NaNO₃) was again equilibrated for 48 h on an orbital shaker, centrifuged and filtered to collect the supernatant for Cu (II) estimation as described in the preceding paragraph. The process was repeated five times.

After each desorption, the amount of Cu remaining adsorbed on biochar (q’_{remaining ads}) was calculated as:

\[
q'_{remaining ads} = \text{Ads. Cu (mg/g)} - \frac{\text{Initial Cu conc. in soln. (mg/L)} - \text{Cu conc. in equil. soln. (mg/L) x Total vol. (mL)}}{\text{Wt. of biochar (g)}}
\]

The experimental data on adsorption-desorption of Cu (II) onto P300 and P450 were fitted to the following Freundlich and Langmuir models (Foo and Hameed, 2010):

**Freundlich model**

\[
q_{ads} = K_F C_e^{1/n}
\]

\[
q'_{remaining ads} = K'_F C_e^{1/n'}
\]

**Langmuir model**

\[
q_{ads} = q_{max} k C_e / (1 + b C_e)
\]

\[
q'_{remaining ads} = q'_{max} k' C_e' / (1 + b' C_e')
\]

Where, q_{ads} and C_e indicate the amount of Cu (II) sorbed by biochar and concentration of Cu (II) in equilibrium solution in
adsorption studies, respectively. The quantities, \( q' \) and \( C_{e}' \) depict the amount of Cu (II) remaining sorbed on biochar after desorption and desorbed concentration of Cu (II) in equilibrium solution, respectively. The values of \( K_F \), \( 1/n \), \( K_F' \) and \( 1/n' \) are Freundlich constants for adsorption and desorption processes, respectively. The values of \( q_{max} \), \( k \), \( q_{max}' \), \( k' \) indicate the adsorption/desorption maxima and constants related to bonding energy terms for Langmuir adsorption-desorption models, respectively.

The suitability of the model fitting was assessed on the basis of coefficient of determination (\( R^2 \) value).

**Results and Discussion**

**General Properties of Pine biochar**

The properties of pine biochar shown in Table 1 clearly indicated that with the increase in pyrolysis temperature, there are decrease in C% and H% and a slight increase in O%. The value of H/C ratio is an indicator of aromaticity of biochar. The analysis showed that this ratio decreased with increase in temperature; indicating that there was higher aromaticity (double or triple bonds) in P450 as compared to P300. This ratio also seems to be a perfect index for predicting the sorption of hydrophobic organic contaminants (HOCs) onto biochars. A linear relationship between H/C and the Freundlich fitting parameters was reported by Chen et al.(2008). The value of O/C ratio is a measure of polarity. Higher ratio indicated presence of more polar functional groups, which could take part in adsorption of Cu (II).

With an increase in pyrolysis temperature, there was an enrichment of basic cations in the ashes, which could be associated with oxides, hydroxides and carbonates of alkali and alkaline earth metals (Yuan et al.2011; Ding et al.2014) along with a reduction in the concentration of acidic surface functional groups (Al-Wabel et al.2013); which might be the plausible reason for higher pH in pine needle biochar produced at higher temperature (450° C). Above 300° C, alkali salts also likely to separate from the organic matrix, increasing the pH of the biochar.

The EC of pine biochars also increased with pyrolysis temperature due to loss of volatile matters, resulting in concentration of oxides of these elements in the ash fraction (Cantrell et al., 2012). Higher mineral ash in P450 could be the probable cause of higher electrical conductivity due to high K content (Joseph et al., 2014).

**Percent removal of Cu (II) from synthetic waste water**

The data on percent removal of Cu (II) affected by P300 and P450 from synthetic waste water are depicted in Fig. 1 which clearly indicates that P450 was more effective in removal of Cu (II) from synthetic waste water compared to P300. For an initial concentration of Cu (II) around 47.7 mg/L, P450 removed 98.1 percent of Cu from waste water while only 41.3% percent could be sorbed by P300. Considering 1.5 mg Cu (II) as the tolerance limit for inland surface water subject to pollution (Class C) as per Indian standards (IS, 1982), P450 might serve as a cheap and effective sorbent for the treatment electroplating waste water containing higher levels of Cu (II).

**Adsorption-desorption isotherm of Cu (II)**

The adsorption-desorption isotherms of Cu (II) onto P300 and P450 at 25°C are depicted in Fig.2. In general adsorption isotherms of Cu(II) onto P300 and P450 were L-type indicating a decrease in adsorption energy
with increasing occupancy of the available adsorption sites. Compared to P300 there was an abrupt initial increase in sorbed amount of Cu (II) onto P450 indicating higher specificity of this sorbent for Cu (II) and the isotherm showed saturation or flattening of the adsorption curve at more than threefold higher adsorption capacity. The desorption isotherms of Cu (II) for P300 and P450 were limited in a very narrow range of desorbed Cu (II) in the equilibrium solution indicating very low reversibility of adsorbed Cu (II). A wider gap between adsorption and desorption isotherms of Cu (II) in the case of P450 indicated very limited desorption of Cu(II) from P450. The values of cumulative desorption of Cu (II) as percentage of adsorbed amount in five cycles of desorption were 8.29 and 1.02 percent for P300 and P450, respectively.

**Table.1** General properties of pine biochars

<table>
<thead>
<tr>
<th>Components</th>
<th>Pine 300</th>
<th>Pine 450</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (%)</td>
<td>61.34</td>
<td>59.89</td>
</tr>
<tr>
<td>H (%)</td>
<td>4.30</td>
<td>3.75</td>
</tr>
<tr>
<td>O (%)</td>
<td>32.38</td>
<td>34.34</td>
</tr>
<tr>
<td>N (%)</td>
<td>1.82</td>
<td>1.86</td>
</tr>
<tr>
<td>H/C</td>
<td>0.84</td>
<td>0.75</td>
</tr>
<tr>
<td>O/C</td>
<td>0.39</td>
<td>0.43</td>
</tr>
<tr>
<td>pH (1:10)</td>
<td>6.17</td>
<td>6.57</td>
</tr>
<tr>
<td>E.C. (µS cm⁻¹) in 1:10 at 25°C</td>
<td>69.51</td>
<td>215.83</td>
</tr>
</tbody>
</table>

**Table.2** Freundlich- and Langmuir- model odelconstants and coefficient of determination for adsorption-desorption of Cu (II) onto pine needle biochars (P300 and P450)

<table>
<thead>
<tr>
<th>Models</th>
<th>Constants</th>
<th>P300</th>
<th>P450</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich adsorption model</td>
<td>KF (mg kg⁻¹)</td>
<td>283.0</td>
<td>1519.2</td>
</tr>
<tr>
<td></td>
<td>1/n</td>
<td>0.2757</td>
<td>0.2396</td>
</tr>
<tr>
<td></td>
<td>R2-value</td>
<td>0.930**</td>
<td>0.934**</td>
</tr>
<tr>
<td>Freundlich desorption model</td>
<td>KF’ (mg kg⁻¹)</td>
<td>877.4</td>
<td>3328.1</td>
</tr>
<tr>
<td></td>
<td>1/n’</td>
<td>0.0074</td>
<td>0.0008</td>
</tr>
<tr>
<td></td>
<td>R2-value</td>
<td>0.796*</td>
<td>0.964**</td>
</tr>
<tr>
<td>Langmuir adsorption model</td>
<td>q max (mg kg⁻¹)</td>
<td>1068.5</td>
<td>3516.0</td>
</tr>
<tr>
<td></td>
<td>k (L kg⁻¹)</td>
<td>0.094</td>
<td>0.741</td>
</tr>
<tr>
<td></td>
<td>R2-value</td>
<td>0.984**</td>
<td>0.996**</td>
</tr>
<tr>
<td>Langmuir desorption model</td>
<td>q’ max (mg kg⁻¹)</td>
<td>893.6</td>
<td>3329.6</td>
</tr>
<tr>
<td></td>
<td>k’ (L kg⁻¹)</td>
<td>149.0</td>
<td>5662.5</td>
</tr>
<tr>
<td></td>
<td>R2-value</td>
<td>0.999**</td>
<td>0.999**</td>
</tr>
</tbody>
</table>

* Significant at p≤0.05, ** Significant at p≤0.01
**Fig. 1** Percent removal of Cu (II) from synthetic waste water by pine biochars (P300 and P450)

**Fig. 2** Adsorption-desorption isotherms of Cu (II) onto pine biochars (P300 and P450)

**Fig. 3** Freundlich (a) and Langmuir (b) adsorption-desorption isotherms of Cu (II) onto pine biochars (P300 and P450)
The computed values of different constants pertaining to Freundlich and Langmuir models along with the coefficient of determination ($R^2$) are presented in Table 2. A close perusal of the values indicated that though both the models could successfully account the adsorption-desorption of Cu (II) onto P300 and P450 however, Langmuir model was the best as this model yielded the highest $R^2$ values (all significant at $p \leq 0.01$). The computed value of adsorption maximum ($q_{\text{max.}}$) and desorption maximum ($q'_{\text{max.}}$) for P450 were more than threefold higher as compared to that of P300. Similarly, the values of constant related to the bonding energy (k and k’) were also higher for P450 as compared to P300 indicating very strong bonding of sorbed Cu (II) onto P450. Hysteresis index (H-index) values calculated from slopes of Freundlich isotherms were 37.3 and 299.5 for P300 and P450, respectively indicating irreversible retention of Cu (II) by pine biochars and the effect was more pronounced in P450 which could be ascribed to more condensed aromatic structure of P450 (Fig. 3).

These findings can be explained by an increase in porosity and surface areas of biochar produced by high temperature pyrolysis (P450), which ultimately increase the adsorption of metals (Chen et al., 2014). It is frequently suggested that high pyrolysis temperatures lead to increased porosity and surface area compared with biochar prepared at low temperature. High incineration temperature also increases the concentration of minerals (K, Ca, Mg and P) on the surface of sorbents that could be used for ion exchange with heavy metals (Chen et al., 2014; Hossain et al., 2011; Subedi et al., 2016). Chen et al., (2011) revealed that biochar from corn straw (600°C) and wood biochar (450°C) had high heavy metal sorption efficiency. The removal of Cu was 56.6% for wood biochar and 98.2% for biochar from corn straw. On the other hand, Komkiene and Baltrenaite (2015) observed that heavy metal ions removal efficiency was about 35–37% on silver birch biochar. Karami et al., (2011) showed that the addition of oak derived biochar in the amount of 20% (v/v) to the soil reduced the Cu sorption by about 69%. On the other hand, Xu and Zhao (2013) proved that biochar from straws of canola and peanut increased the Cu sorption capacity of three soils (Oxisol and Ultisol) by about 54.2% and 102.1%, when 3 and 5% of biochar were added. Considering these works, it could be anticipated that above variations in results might result from the differences in nature of the feedstock and pyrolysis temperature.

In conclusion the biochar derived from the pyrolysis of pine needles at 300 and 450°C varied in general properties as well as Cu (II) sorption characteristics. Pine biochar prepared by pyrolysis at 450°C had higher sorption capacity for Cu (II) compared to pine biochar pyrolyzed at 300°C. Adsorption-desorption data of Cu (II) onto pine biochar closely conformed to Langmuir model. Pine biochar prepared by pyrolysis at 450°C can serve as a potential cost effective sorbent for the treatment of Cu (II) waste water generated from electroplating industries.

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