Effect of iron treatment and equilibrium pH on the kinetics of removal of some substituted phenols from synthetic wastewater onto *Nostoc* sp. biomass

Namrata Gururani, Devesh Bhatt, Anjana Srivastava and Prakash Chandra Srivastava

**ABSTRACT**

Substituted phenols, such as 4-Nitrophenol (4-NP) and 2,4-Dichlorophenol (2,4-DCP), that are present in industrial wastewaters are considered as priority pollutants due to their toxic effects. Their removal by biosorption presents an eco-friendly, cost-effective method. The kinetics of removal of 4-NP and 2,4-DCP by untreated *Nostoc* sp. (UNB) and Fe-treated *Nostoc* sp. biomass (FNB) were studied at three different pH (4.0, 7.0 and 9.0). The highest sorption of both phenols (2.28 mg 4-NP and 1.51 mg 2,4-DCP g$^{-1}$) coupled with the lowest cumulative percentage desorption was recorded with FNB at pH 7.0. The sorption of both phenols by UNB and FNB was best accounted for by pseudo-second-order kinetics. Compared to UNB, FNB had significantly higher equilibrium sorption capacities for both phenols at all the three pH values and also higher sorption rate constants of 4-NP at pH 4 and 9 and of 2,4-DCP at pH 4 and 7. The Fourier transform infrared spectroscopy (FTIR) analysis showed that $–\text{OH}$ and $\text{COO}^{'-}$ groups of UNB interacted with Fe$^{3+}$. The sorption of 4-NP and 2,4-DCP on UNB was likely through H-bonding/structural cation bridging with the phenolic group, while their sorption onto FNB appeared to be a complexation reaction with very low reversibility.

**Key words** | 2,4-Dichlorophenol, 4-Nitrophenol, adsorption kinetics, biosorption, *Nostoc* sp.

**HIGHLIGHTS**

- The kinetics of removal of two priority pollutants, 4-Nitrophenol (4-NP) and 2,4-Dichlorophenol (2,4-DCP) was studied on untreated and Fe treated *Nostoc* sp. at three different pH.
- The highest sorption of both the substituted phenols was recorded on Fe-treated *Nostoc* sp. biomass at pH 7.
- Sorption of both the phenols was best accounted for by pseudo-second-order kinetics.
- FTIR analysis showed the interaction of hydroxyl ($–\text{OH}$) and carboxylate ($\text{COO}^{'-}$) groups of *Nostoc* sp. with Fe$^{3+}$.
- Scanning electron microscope (SEM) images revealed deposition of Fe on *Nostoc* sp. biomass surfaces.

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INTRODUCTION

Phenols and substituted phenols are undesirable by-products of many industries (pharmaceutical, textile, petroleum, paint, pulp and paper etc) that are released in wastewater effluents. Their concentrations have been reported to reach 1,000 μgL⁻¹ (Rao & Viraraghavan 2002). These organic compounds cause pollution of groundwater and other water resources and their exposure may cause damage to the nervous, renal and circulatory systems (Ramírez et al. 2017). The US Environmental Protection Agency (EPA), for example, has listed 11 phenols as priority pollutants for all living organisms (Angelino & Gennaro 1997). The EPA has also fixed the limit of these substituted phenols to less than 1 mg L⁻¹ in treated effluents (Balasubramanian & Venkatesan 2005). Para or 4-Nitrophenol can cause blood disorders, mutagen activity and direct burns on skin and eyes in humans and other animals (Cooper et al. 1997). Chlorophenols are harmful if ingested and are absorbed through the skin, causing cell necrosis and cancer in the human body (Igbinosa et al. 2013). Chlorophenols in water do not easily biodegrade and impart a bad odour and taste to water (Heydaripour et al. 2019). Both nitrophenols and chlorophenols cause acute and chronic toxicity in humans (Navarro et al. 2008; Lee et al. 2013).

The removal of these toxic substances from polluted wastewater or reducing their concentrations to the permitted levels as specified by environmental standards is a tedious process due to their water-soluble nature (Angelino & Gennaro 1997). Different methods such as membrane filtration (Mehrizad et al. 2012), degradation (Qiu et al. 2012; Xiong et al. 2012), adsorption (Abburi 2003; Navarro et al. 2008; Yuan-Xiang et al. 2014; Karri et al. 2017a, 2017b; Hairuddin et al. 2019), and chemical reduction (Fan et al. 2012; Jin et al. 2012) have been suggested for the removal of phenolic compounds from contaminated waters. The current interest of the scientific community has now shifted towards biological methods for the remediation of environmental pollutants (Karatay et al. 2017). Microorganisms are currently gaining importance as biosorbents for the removal of pollutants from wastewaters. As compared to bacteria and fungi, cyanobacteria are preferred, owing to many desirable features, such as simple nutrient requirements and no generation of harmful substances (Gupta & Rastogi 2008; Abed et al. 2009). The biological oxygen demand (BOD) of cyanobacteria is also lower, making them more efficient for the biodegradation of aromatic pollutants in effluents (Karigar et al. 2006).

Aksu & Yener (2001) attempted biosorption for the treatment of organic pollutants. Recently, Karatay et al. (2017) examined the biosorption capacity of Phormidium sp. for phenol and reported that the adsorption was almost 100% at pH 7. Among cyanobacteria, Nostoc sp., with cells arranged in bead-like chains that are grouped together in a gelatinous mass of polysaccharides and other organic substances (Sand-Jensen 2014), present an ideal biological
material for the biosorption of environmental pollutants in nature. Dried *Nostoc* sp. biomass has also been tried as a biosorbent for the removal of heavy metals (Singh & Balomajumder 2016). However, no information is available in the literature on the use of *Nostoc* sp. as a biosorbent for priority pollutants like 4-NP and 2,4-DCP.

Since many active functional groups like hydroxyl (OH⁻), carbonyl (>C = O), carboxyl (COOH⁻), sulphate (SO₄²⁻) moieties are present in the mucilage sheath of cyanobacteria (Tease & Walker 1987), we thought of modifying the mucilage sheath of dry *Nostoc* sp. biomass by treating it with FeCl₃ to study the sorption properties of untreated (UNB) and Fe³⁺-treated *Nostoc* sp. biomass (FNB) for some phenols. Considering the possibility that polluted industrial effluent might contain admixtures of substituted phenols like 4-NP and 2,4-DCP (Al Hashemi et al. 2015), the present investigation was undertaken to examine the kinetics of biosorption of both 4-NP and 2,4-DCP onto UNB and FNB at three different pH values. Scanning electron microscopy and infrared spectroscopy were also performed to study the effect of Fe³⁺ treatment on sorption surface(s) and the involvement of different functional groups in holding Fe³⁺ ions and phenolic pollutants.

**MATERIAL AND METHODS**

Analytical grade 4-Nitrophenol (4-NP) and 2,4-Dichlorophenol (2,4-DCP) were procured from Sigma Aldrich. The pure culture of *Nostoc* sp. was obtained from ICAR-National Bureau of Agriculturally Important Microorganisms (NBAIM) culture centre located in Mau Nath Bhanjan, Uttar Pradesh, India. All reagents used in the study were of analytical or high-performance liquid chromatography (HPLC) grade and were procured from Sigma Aldrich and S.D. Fine Chem. Ltd, Mumbai. The buffer solutions used in the study were prepared as follows: 830 mL of 0.2 M acetic acid + 170 mL of 0.2 M sodium acetate solution L⁻¹ for pH 4.0, 500 mL of 0.2 M KH₂PO₄ + 300 mL of 0.2 M KOH L⁻¹ + 100 mL water for pH 7.0 and 800 mL of 0.05 M borax + 200 mL of 0.05 M boric acid L⁻¹ for pH 9.0. All the buffers were stored in a refrigerator (1–2 °C). Double-distilled water was used to make all solutions.

**Biosorbert growth conditions and their modification**

*Nostoc* sp. was cultured in BG-11 medium as outlined by Ahad et al. (2017). The culture was inoculated in 100 mL conical flasks containing the medium and the pH was maintained at 7.2. The flasks were incubated for 7–10 days at 24 °C with 16 hours of light and 8 hours of darkness. FNB was prepared by equilibrating 2 g untreated dry biomass of *Nostoc* sp. with 25 mL of 0.1 M FeCl₃ solution (pH 6.4) for 24 hours. Then, the contents were filtered and subjected to multiple washings using distilled water. After filtration, both UNB and FNB were dried in an electric oven at 40 °C. Fifty mg each of dried UNB and FNB were digested in 10 mL di-acid (HNO₃: HClO₄, 5:1 v/v) and the digests were diluted to 25 mL using double-distilled water. The extracts were assayed for total iron content using atomic absorption spectrophotometry (GBC Avanta M, Australia). The total iron contents in UNB and FNB were 3.23 ± 0.22 mg and 18.21 ± 0.16 mg g⁻¹ dry weight, respectively.

**Kinetics of biosorption studies**

Biosorption studies were carried out by the batch method at pH 4.0, 7.0 and 9.0. Ten mg of the dried biomass of UNB or FNB was taken in a series of centrifuge tubes for each time interval in duplicate and 0.8 mL of a stock solution containing 50 mg of each of the two substituted phenols (4-NP and 2,4-DCP) L⁻¹. The final volume of solution in the centrifuge tube was maintained to 20 mL by adding the requisite volume of the respective buffer solution of pH 4.0, 7.0 and 9.0.

The centrifuge tubes were kept in an orbital shaker at 120 rpm for different time intervals: 0, 1, 2, 3, 4, 6, 8, 12, 24 and 48 hours. After each time interval, duplicate centrifuge tubes were centrifuged at 5,000 rpm for 10 min and a clear supernatant was decanted in glass tubes and stored in the refrigerator (1–2 °C) until HPLC analysis. To check the reversibility (desorption) of phenols sorbed onto UNB or FNB after 12 hours of equilibration, 20 mL of the respective buffer solution (pH 4.0, 7.0 and 9.0) was added to the centrifuge tube containing biomass pellets, cyclo-mixed and equilibrated at 120 rpm for 1 hour. The contents were centrifuged to obtain a clear supernatant as described. The desorption process was repeated five times to find the total desorbed quantity of substituted phenols from both UNB and FNB.

**Analytical method used for estimation**

The concentration of 4-NP and 2,4-DCP was analyzed by HPLC (Dionex Ultimate 3,000 model). The HPLC conditions maintained were: RP C₁₈ column, 250 × 4.6 mm
i.d., 5 μm particle size, mobile phase was methanol:water (80:20) in isocratic mode at a flow rate of 1 mL min⁻¹ and UV detection was done at 300 nm. Each solution was passed through 0.45 μm polytetrafluoroethylene (PTFE) disc filter before injection. The injection volume was 20 μL. The retention times of 4-NP and 2,4-DCP were determined and found to be 3.9 and 6.2 min, respectively. The concentration of 4-NP and 2,4-DCP in the supernatant solution were computed from standard curves prepared in the range of 0.1 to 8.0 mg 4-NP or 2,4-DCP L⁻¹. In the sorption study, the sorbed amount of both substituted phenols (Q) on UNB and FNB was calculated as:

\[
Q (\text{mg/g}) = \frac{(C_0 - C_e) \times \text{Total volume (mL)}}{w}
\]

(1)

where, Co and Ce were the initial and final concentrations of 4-NP or 2,4-DCP in μg mL⁻¹ and w was initial weight of UNB or FNB in mg. In the desorption study, the cumulative percentage desorption of 4-NP or 2,4-DCP was calculated as:

\[
\text{Cumulative percentage desorption} (%) = \frac{\sum (C_t \times \text{Total volume (mL)})/w}{Q} \times 100
\]

(2)

where, C_t was desorbed concentration of 4-NP or 2,4-DCP in μg mL⁻¹, w was initial weight of UNB or FNB in mg and Q was sorbed amount of 4-NP or 2,4-DCP in mg/g.

Infrared spectroscopy

Ten mg of both UNB and FNB were treated with 2 mL of 50 mg L⁻¹ of 4-NP or 2,4-DCP for 12 hours separately, followed by filtration, washing and drying. Fourier transformed infrared spectra (FTIR) of pure 4-NP or 2,4-DCP and both UNB and FNB samples before and after sorption of phenols were obtained using a Bruker FTIR spectrometer (Alpha model, Germany).

Scanning electron microscopy

The morphology and surface changes of UNB and FNB were studied after gold coating using JFC Model-1600 and scanning electron microscope (SEM) images were recorded using a JEOL-JSM (Model No. 6610).

Statistical analysis

The data on kinetics of sorption of 4-NP and 2,4-DCP were fitted to different kinetic models using regression analysis, and computed values of constants from the best-fitting model were compared by paired t-test at the 5% level of significance using the standard computer program software developed by the Department of Mathematics, Statistics, and Computer Science of G. B. Pant University of Agriculture and Technology, Pantnagar, India.

RESULTS AND DISCUSSION

Kinetics of biosorption

In general, the biosorption of both the substituted phenols (4-NP and 2,4-DCP) increased with time and reached near equilibrium at 12 hours. With an increase in time beyond 12 hours, further increases in sorption of both phenols was relatively small at all three pH values (Figure 1). In all the cases, a higher amount of 2,4-DCP was initially sorbed as compared to 4-NP, but near equilibrium the sorbed quantity of 4-NP was higher than 2,4-DCP. With UNB, the final sorbed amounts of 4-NP were 1.380, 2.081 and 1.357 mg g⁻¹ while with FNB these amounts were 1.678, 2.229 and 1.646 mg g⁻¹ at equilibrium pH 4.0, 7.0 and 9.0, respectively. On the other hand, with UNB the final sorbed amounts of 2,4-DCP were 1.286, 1.433 and 1.176 mg g⁻¹ while with FNB these amounts were 1.420, 1.505 and 1.396 mg g⁻¹ at equilibrium pH 4.0, 7.0 and 9.0, respectively. Therefore, the highest sorption of both substituted phenols by UNB or FNB was at equilibrium pH 7.0 and irrespective of the pH value, the sorption of both substituted phenols at the equilibrium was higher for FNB as compared to UNB. Karatay et al. (2017) also reported the maximum biosorption of phenol, a primary priority pollutant, on Phormidium sp. at pH 7.

The cumulative percentage desorption of sorbed quantities of both substituted phenols from UNB and FNB at different pH values are depicted in Figure 2. From UNB, the percentage desorption of 4-NP was higher than 2,4-DCP and it was the highest for both the phenols at pH 9.0 followed by pH 4.0, so the lowest desorption was recorded at pH 7.0. For FNB, the percentage desorption of 4-NP was similar (0.69%) at pH 4.0 and 9.0 but the lowest (0.47%) at pH 7.0. However, the percentage desorption of 2,4-DCP for FNB was only 0.37% at pH 4.0 but it was non-detectable (0.0%) at pH 7.0 and 9.0, indicating an irreversible bonding of this phenol with Fe³⁺ ions present on
**Figure 1** Sorption of 4-NP and 2,4-DCP onto untreated (UNB) and Fe-treated Nostoc sp. biomass (FNB) at equilibrium pH of 4.0, 7.0 and 9.0 at different time intervals.

**Figure 2** Percentage cumulative desorption of 4-NP and 2,4-DCP sorbed onto untreated (UNB) and Fe-treated Nostoc sp. biomass (FNB) at equilibrium pH of 4.0, 7.0 and 9.0. The numerical values placed above the histograms indicate percentage cumulative desorption ± standard error; nd: stands for non-detectable desorption.
the FNB surface. Mukherjee et al. (2017) also recorded irreversible binding of fluoride ions by Nostoc sp. due to binding with Ca$^{2+}$ ions.

Nostoc sp. trichomes are known to be enclosed in mucilaginous external layers which are composed of both capsular and released polysaccharides, including several neutral sugars, gluco- and gluco-uronic acids, along with some proteins (Li et al. 2001). The point of zero charge (pH$_{ZPC}$) of untreated Nostoc sp. biomass has been reported to be approximately 5.0 (Mukherjee et al. 2017) and it can retain Fe$^{3+}$ in exchange for H$^+$ from –COOH and protonated –OH (Anjana et al. 2007) and NH$_2$ moieties from cyanobacterial surface(s). Both UNB and FNB could be expected to bear a net positive charge at pH 4.0 but a net negative charge at pH 7.0 and 9.0.

Among the substituted phenols chosen for the study, in the 4-NP molecule the nitro group, being an electron withdrawing group, pulls electron density towards itself, resulting in an increased electron delocalization and resonance thereby stabilizing the 4-NP molecule. In 2,4-DCP, the chloro groups, having decreased delocalisation as compared to nitro group, do not provide such stability (Navarro et al. 2008). The position of an electron withdrawing group like a chloro group at the ortho-position near a phenolic (OH$^-$) group in 2,4-DCP exerts a greater influence on the sorption ability of the sorbate due to steric hindrance in H-bonding (Boyd 1982). The dissociation constant (pK) of 4-NP is 7.15 while that of 2,4-DCP is 7.89.

In the light of these facts, the anticipated mechanism of sorption of these two substituted phenols onto UNB and FNB surfaces at different pH values could be as follows. At pH 4.0, the UNB sorption surface is positively charged and both the phenols, having high electron density groups, might form H-bonds with OH$^-$ and COOH$^-$ groups on Nostoc sp. surface(s) with some degree of desorption; the percentage desorption is likely to be higher for 4-NP, which is likely to be retained in a multi-molecular layer. At pH 7.0, the UNB sorption surface is likely to be negatively charged due to partial dissociation of some structural groups of biomass, and 4-NP, having pK value of 7.15, will also dissociate to form a phenoxide anion, which may get additionally sorbed through cation bridging with some structural cations present in the mucilaginous mass of Nostoc sp.; 2,4-DCP will exist pre-dominantly as undissociated molecule. At pH 9.0, the UNB sorption surface is likely to be negatively charged and both substituted phenols, 4-NP and 2,4-DCP, existing as phenoxide anions, are likely to face higher electrostatic repulsion from the sorption surface and competition from OH$^-$ ions (Ahmaruzzaman 2008). In the case of FNB, both substituted phenols, which exist as undissociated molecules at pH 4.0, as the 4-NP anion and undissociated 2,4-DCP at pH 7.0 and as phenoxide anions of both 4-NP and 2,4-DCP at pH 9.0, may form a surface complex with Fe$^{3+}$ (Islam et al. 2015) resulting in very low desorption of sorbed phenols.

Kinetic models

The sorption data of 4-NP and 2,4-DCP onto UNB and FNB were fitted to different kinetic models. The observation obtained for 0 hours’ shaking was assigned a time of 0.166 hour considering the contact time of both phenols with sorbent during centrifugation (10 min).

Zero-order model \[ Q_t = Q_0 + k_0 t \]  (3)

Pseudo-first-order model \[ \ln(Q_e - Q_t) = \ln Q_e - k_0 t \]  (4)

First-order model \[ \ln Q_t = \ln Q_e - k_1 t \]  (5)

Pseudo-second-order model \[ t/Q_t = (1/k_2 Q_e^2) + t/Q_e \]  (6)

Second-order model \[ 1/Q_t = 1/Q_e - k_2 t \]  (7)

where $Q_0$, $Q_t$ and $Q_e$ indicate the quantity of adsorbate (mg g$^{-1}$) at 0, t and equilibrium time in hours, respectively. The constants, namely: $k_0$ (h$^{-1}$), $k_{01}$ (h$^{-1}$), $k_1$ (h$^{-1}$), $k_{02}$ (g mg$^{-1}$ h$^{-1}$) and $k_2$ (g mg$^{-1}$ h$^{-1}$) indicate the rate constants for the zero-, pseudo-first-, first-, pseudo-second- and second-order models, respectively. The goodness of data fitting to a model was examined by linear coefficient of determination ($R^2$).

It is clearly evident from the data in Table 1 that the pseudo-second-order model gave the best fit for all the cases with the highest values of $R^2$; all significant at $p \leq 0.01$. Wang et al. (2007) also noted that the pseudo-second-order model gave the best fit for the adsorption data of 2,4-DCP on activated carbon. Mukherjee et al. (2017) also reported that the biosorption of fluoride ions onto Nostoc sp. followed the pseudo-second-order kinetic model. Among other kinetic models, the pseudo-first-order model could also appreciably account (significant at $p \leq 0.01$) for the sorption kinetics in the case of 4-NP and 2,4-DCP for both UNB and FNB but to a much lesser degree as compared to pseudo-second-order model. The zero-order model could account for sorption of 4-NP by both UNB and FNB but the $R^2$ values were significant only at $p \leq 0.05$. The first-order model could only account for sorpitions of 4-NP by UNB at pH 4.0 and 9.0 and by FNB at pH 7.0 but $R^2$ values were significant only at
Table 1 | The estimated sorbed amounts, rate constants and R² values with different kinetic models for sorption of 4-NP onto untreated (UNB) and Fe³⁺-treated Nostoc sp. biomass (FNB) at different equilibrium pH

<table>
<thead>
<tr>
<th>Equilibrium pH</th>
<th>Kinetic model</th>
<th>UNB</th>
<th>Rate constant (k)</th>
<th>R² – value</th>
<th>FNB</th>
<th>Rate constant (k)</th>
<th>R² – value</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>Zero order</td>
<td>0.876</td>
<td>0.0145</td>
<td>0.520a</td>
<td>1.217</td>
<td>0.0138</td>
<td>0.400a</td>
</tr>
<tr>
<td></td>
<td>Pseudo-first order</td>
<td>0.897</td>
<td>0.2213</td>
<td>0.931**</td>
<td>0.662</td>
<td>0.2099</td>
<td>0.901**</td>
</tr>
<tr>
<td></td>
<td>First order</td>
<td>0.849</td>
<td>0.0143</td>
<td>0.457**</td>
<td>1.183</td>
<td>0.0106</td>
<td>0.350</td>
</tr>
<tr>
<td></td>
<td>Pseudo-second order</td>
<td>1.419</td>
<td>0.6000a</td>
<td>0.998**</td>
<td>1.707b</td>
<td>0.8462b</td>
<td>1.000**</td>
</tr>
<tr>
<td></td>
<td>Second order</td>
<td>0.822</td>
<td>0.0147</td>
<td>0.381</td>
<td>1.146</td>
<td>0.0085</td>
<td>0.298</td>
</tr>
<tr>
<td>7.0</td>
<td>Zero order</td>
<td>1.341</td>
<td>0.0219</td>
<td>0.448**</td>
<td>1.466</td>
<td>0.0226</td>
<td>0.451**</td>
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<tr>
<td></td>
<td>Pseudo-first order</td>
<td>1.513</td>
<td>0.2775</td>
<td>0.984**</td>
<td>1.503</td>
<td>0.2714</td>
<td>0.959**</td>
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<tr>
<td></td>
<td>First order</td>
<td>1.281</td>
<td>0.0146</td>
<td>0.387</td>
<td>1.410</td>
<td>0.0138</td>
<td>0.402**</td>
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<td>Pseudo-second order</td>
<td>2.131b</td>
<td>0.4387b</td>
<td>0.999**</td>
<td>2.289k</td>
<td>0.4146a</td>
<td>0.999**</td>
</tr>
<tr>
<td></td>
<td>Second order</td>
<td>1.220</td>
<td>0.0104</td>
<td>0.319</td>
<td>1.356</td>
<td>0.0089</td>
<td>0.350</td>
</tr>
<tr>
<td>9.0</td>
<td>Zero order</td>
<td>0.500</td>
<td>0.0243</td>
<td>0.579**</td>
<td>1.162</td>
<td>0.0139</td>
<td>0.441**</td>
</tr>
<tr>
<td></td>
<td>Pseudo-first order</td>
<td>1.728</td>
<td>0.2520</td>
<td>0.911**</td>
<td>0.448</td>
<td>0.0645</td>
<td>0.612**</td>
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<tr>
<td></td>
<td>First order</td>
<td>0.405</td>
<td>0.0360</td>
<td>0.426**</td>
<td>1.129</td>
<td>0.0111</td>
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<td>Pseudo-second order</td>
<td>1.515</td>
<td>0.1425a</td>
<td>0.984**</td>
<td>1.665a</td>
<td>0.7730b</td>
<td>0.999**</td>
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<tr>
<td></td>
<td>Second order</td>
<td>0.315</td>
<td>0.0766</td>
<td>0.236</td>
<td>1.091</td>
<td>0.0093</td>
<td>0.280</td>
</tr>
</tbody>
</table>

The best-fitting pseudo-second-order constants at different equilibrium pH with dissimilar letters in the superscript within a column indicate statistically significant differences by the paired t-test.

†Rate constant (k) values mentioned against zero-, pseudo-first-, first-, pseudo-second- and second-order kinetic models are k₀₁ (h⁻¹), k₀₂ (h⁻¹), k₁ (h⁻¹), k₂o (g mg⁻¹ h⁻¹) and k₂ (g mg⁻¹ h⁻¹), respectively.

**Significant at p < 0.01. *Significant at p < 0.05. The best-fitting pseudo-second-order constants at a given equilibrium pH with bold numerals in a row indicate statistically significant differences between UNB and FNB by the paired t-test.

p ≤ 0.05. The second-order model failed to account for sorption of both the phenols by UNB and FNB.

In general, the estimated value of sorbed 4-NP at equilibrium (Qₑ) for both UNB and FNB as per pseudo-second-order kinetics increased with the increase in pH from 4.0 to 7.0 but decreased at pH 9.0 (Table 1). At all three pH values, the estimated values of Qₑ for FNB were significantly higher than their corresponding values for UNB at pH 4.0 and 7.0 but no significant difference was recorded at pH 9.0. Irrespective of Fe treatment of biomass, the relatively lower k₀₂ at pH 9.0 could be attributed to the dominance of Fe₃⁺ complexation.

The FTIR spectra for UNB and FNB are presented in Figure 3. In the spectrum of UNB, O-H stretching vibrations further decreased with the increase in pH to 9.0. The estimated k₀₂ values for FNB were statistically and significantly higher than their corresponding values for UNB at pH 4.0 and 7.0 but no significant difference was recorded at pH 9.0. Irrespective of Fe treatment of biomass, the relatively lower k₀₂ at pH 9.0 could be attributed to the dominance of Fe₃⁺ complexation.
of free hydroxyl –OH groups in carbohydrates appeared as a broad peak from 3,844.54 cm⁻¹ while the peak at 3,273.95 cm⁻¹ indicated O-H stretching of –OH groups in polymeric association. A peak at 2,922.13 cm⁻¹ was assigned to C-H stretching vibrations of the aliphatic –CH₂ groups in carbohydrates and proteins present in the mucilaginous sheath of the algae. The peak noted at 1,628.28 cm⁻¹ corresponded to the ring stretching of mannose or galactose sugars. The absorption peaks at 1,538.43 and 1,241.33 cm⁻¹ could be attributed to the stretching of the COO⁻ group. A strong absorption at 1,017 cm⁻¹ was due to the vibration of C-O-O and C-O in carbohydrates.

Table 2  The estimated sorbed amounts, rate constants and R² values with different kinetic models for the sorption of 2,4-DCP on untreated (UNB) and Fe³⁺-treated Nostoc sp. biomass (FNB) at different equilibrium pH

<table>
<thead>
<tr>
<th>Equilibrium pH</th>
<th>UNB</th>
<th>FNB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sorbed amount (mg/g)</td>
<td>Rate constant¹ (k)</td>
</tr>
<tr>
<td>4.0</td>
<td>Zero order 1.140</td>
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The best-fitting pseudo-second-order constants at different equilibrium pH with dissimilar letters in the superscript within a column indicate statistically significant differences by the paired t-test.

¹Rate constant (k) values mentioned against zero-, pseudo-first-, first-, pseudo-second- and second-order kinetic models are k₀ (h⁻¹), k₀₁ (h⁻¹), k₁ (h⁻¹), k₀₂ (g mg⁻¹ h⁻¹) and k₂ (g mg⁻¹ h⁻¹), respectively.

**significant at p – 0.01, *significant at p – 0.05. The best-fitting pseudo-second-order constants at a given equilibrium pH with bold numerals in a row indicate statistically significant differences between UNB and FNB by the paired t-test.

Figure 3  FTIR spectra of untreated (UNB) and Fe-treated (FNB) Nostoc sp. biomass.
As compared to UNB, in the FTIR spectrum of FNB, there was a diminution of the peak at 3,844 cm\(^{-1}\) and a decrease in absorption and shifting of the peaks from 3,273.95 to 3,270.75 cm\(^{-1}\), from 1,558.43 to 1,531.97 cm\(^{-1}\) and from 1,241.33 to 1,233.91 cm\(^{-1}\), which clearly indicated that Fe treatment of \textit{Nostoc} sp. had led to the association of Fe\(^{3+}\) with -OH and \(-\text{COO}^-\) structural groups of \textit{Nostoc} sp. biomass. Cyanobacterial exopolysaccharides have been reported to biosorb metals by complex formation with C=O, COOH, OH and sulphate groups (Tease & Walker 1987).

A broad band feature of 4-NP at 3,318.34 cm\(^{-1}\) assigned to -OH stretching vibrations (4-NP) shifted to 3,268.18 cm\(^{-1}\) for 4-NP sorbed onto UNB and to 3,263.01 cm\(^{-1}\) for 4-NP sorbed onto FNB. The shift to the lower wave number indicated bonding of an -OH group of 4-NP onto the sorption surface (Figure 4). A shoulder at 1,570 cm\(^{-1}\) appeared due to N-O stretching and this shoulder disappeared in the spectra of 4-NP sorbed onto both UNB and FNB due to the formation of what was possibly a multi-molecular layer on the sorbate surface. Other peaks at 2,942.86 and 2,830.69 cm\(^{-1}\) were due to C-H stretching vibrations in 4-NP which were largely diminished after 4-NP sorption onto UNB or FNB due to the restricted stretching of sorbed molecules. The absorbance due to C=C multiple bond stretching in the aromatic ring of 4-NP at 1,449.68 cm\(^{-1}\) (4-NP) was decreased after the sorption onto both UNB and FNB. A sharp peak due to C-O stretching in the phenolic group of 4-NP at 1,020.44 cm\(^{-1}\) suffered a decrease in absorption as well as a shift to a lower wave number; 1,014.01 cm\(^{-1}\) after 4-NP sorption on to UNB and to 1,010.66 cm\(^{-1}\) for FNB due to bonding of phenolic group with the sorption surface.

The FTIR spectra of 2,4-DCP before and after sorption onto UNB and FNB showed that the -OH stretching vibration peak of 2,4-DCP at 3,317.57 cm\(^{-1}\)shifted to 3,270.15 cm\(^{-1}\) and to 3,264.11 cm\(^{-1}\), respectively, besides a decrease in absorbance due to the bonding of the phenolic group on sorption surfaces (Figure 5). Further, a C-H stretching vibration peak of 2,4-DCP at 2,942.59 cm\(^{-1}\) shifted to 2,921.18 cm\(^{-1}\) and 2,881.04 cm\(^{-1}\) with decreased absorbance after sorption onto UNB and FNB, respectively, and this could for the same reason as for 4-NP. A sharp band due to C-O stretching in the phenolic group recorded at 1,020.71 cm\(^{-1}\) for 2,4-DCP shifted to 1,015.00 cm\(^{-1}\) for 2,4-DCP sorbed onto UNB and to 1,012.01 cm\(^{-1}\) for 2,4-DCP sorbed onto FNB; this clearly showed the involvement of the phenolic (-OH) group of 2,4-DCP in bonding to the sorption surface.

**SEM analysis**

SEM images of UNB and FNB are shown in Figure 6. The image of UNB (a) showed highly rugged surface due to the presence of highly interwoven mucilage fibrils. After Fe
treatment of the *Nostoc* sp. biomass, the surface appeared to
be less rugged with clear metal deposition(s) on surface fibrils and depressions.

**CONCLUSIONS**

*Nostoc* sp. biomass can effectively remove both 4-Nitrophenol and 2,4-Dichlorophenol from wastewater by biosorption. Iron treatment of *Nostoc* sp. biomass increased the sorption capacity of the biomass for both pollutants with very low desorption. The highest sorption of both phenols by UNB and FNB was recorded at neutral pH. The sorption reaction of both substituted phenols followed pseudo-second-order kinetics. FTIR spectra revealed that Fe treatment of the biomass resulted in bonding of Fe$^{3+}$ ions with hydroxyl- and carboxylate groups of *Nostoc* sp. biomass. The sorption of both substituted phenols occurred due to H-bonding/structural cation bridging of the phenolic (–OH) group on UNB and additional complexation reactions on FNB. The *Nostoc* sp. biomass, especially after treatment with iron, may serve as an excellent adsorbent for the removal of priority pollutant phenols from contaminated waters. The recovery of sorbed phenolic compounds can also be attempted for their recycling or safe disposal.
REFERENCES


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waste by adsorption onto nano-titanium dioxide.


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