Removal of Ni(II) and Cu(II) from aqueous solutions using ‘green’ zero-valent iron nanoparticles produced by oak and mulberry leaf extracts


ABSTRACT

The production of zero-valent iron nanoparticles, using extracts from natural products, represents a green and environmentally friendly method. Synthesis of ‘green’ zero-valent nanoparticles (nZVI) using oak and mulberry leaf extracts (OL-nZVI and ML-nZVI) proved to be a promising approach for Ni(II) and Cu(II) removal from aqueous solutions. Characterization of the produced green nZVI materials had been conducted previously and confirmed the formation of nanosize zero-valent iron particles within the size range of 10–30 nm, spherical with minimum agglomeration observed by transmission electron microscopy and scanning electron microscope morphology measurements. Batch experiments revealed that the adsorption kinetics followed a pseudo-second-order rate equation. The obtained adsorption isotherm data could be well described by the Freundlich model and OL-nZVI showed higher adsorption capacity for Ni(II) removal than ML-nZVI, while ML-nZVI adsorption capacity was higher for Cu(II). In addition, investigation of the pH effect showed that varying the initial pH value had a great effect on Ni(II) and Cu(II) removal. Adsorbed amounts of Ni(II) and Cu(II) increased with pH increase to pH 7.0 and 8.0. This study indicated that nZVI produced by a low-cost and non-toxic method with oak and mulberry leaf extracts could be used as a new material for remediation of water matrices contaminated with Ni(II) and Cu(II).

Key words | green adsorbent, Ni(II) and Cu(II) removal, oak and mulberry leaves, zero-valent iron nanoparticles

INTRODUCTION

Nickel and copper, heavy metals, when discharged into the environment, will have detrimental effects on the biosphere. Nickel can be present in wastewater from the electroplating, refining and welding industries (Efecan et al. 2009; Kumar et al. 2011). Excessive levels of nickel in water can affect biosystems and pose a threat to human beings. The toxicity of nickel causes adverse health effects such as cancer, skin allergy and lung fibrosis (Nordberg et al. 2014). The most important health problem due to nickel and its compounds are allergic dermatitis (nickel itch) and increased incidence of cancers (Schaumlöffel 2012; Nordberg et al. 2014). Copper is a heavily used metal in industries such as plating, mining and smelting, brass manufacture, electroplating, and petroleum refining and in the excessive use of Cu-based agrichemicals mining (Huang & Su 2010; Igberase et al. 2014; Bakhtiari & Azijian 2015). These industries produce much wastewater and sludge containing Cu(II) ions with various concentrations, which have negative effects on the water environment. Copper may also be found as a contaminant in food, especially shellfish, liver, mushrooms and nuts. It has been reported that excessive intake of copper by humans may lead to severe mucosal irritation, hepatic and renal damage, widespread capillary damage and central nervous system problems (Demirbas et al. 2009; Nordberg et al. 2014). Hence the removal of nickel(II) and copper(II) from water and wastewater is highly essential.

The application of nanoparticles of zero-valent iron (nZVI) as a reducing agent has been widely reported in environmental remediation in recent years (Zhang et al. 2010; Shi et al. 2011; Fu et al. 2013; Qu et al. 2015). Due to
their high specific surface area and high reactivity, nZVIs can remove various contaminants from water. Methods for the production of nanoparticles via chemical synthesis have several limitations and problems such as the toxicity of the chemicals used and toxic byproducts, which are often potentially dangerous to the environment (Shahwan et al. 2011). These limitations have led to the use of ‘greener’ solvents, extracts of natural products with high antioxidant capacities, such as green tea leaves (Chrysochoou et al. 2012; Abbassi et al. 2015; Weng et al. 2015), oolong tea leaves (Huang et al. 2014), pomegranate, mulberry and cherry (Machado et al. 2015) for nZVI synthesis. The plant extracts have proven to be non-toxic to living organisms, a reproducible resource and environmentally friendly materials containing polyphenols which act as both reducing and stabilizing agents when they are used for ‘green’ synthesizing of nZVI and prolonging their reactivity (Nadagouda et al. 2010; Weng et al. 2015).

The main advantages of this method are the lower toxicity of the used reducing agent compared to borohydride, and the valorization of natural products that, in some cases, are considered waste or do not have any added value. Additionally, these extracts have high water solubility, low toxicity and can act as a nutrient source which can enhance complementary biodegradation (Nadagouda et al. 2010; Hoag et al. 2009; Machado et al. 2013). Nadagouda et al. (2010) compared the nZVIs produced using the green and borohydride methods and observed that some of the green nZVIs were found to be non-toxic when compared with control samples prepared using the conventional borohydride reduction protocols. The absence of studies and knowledge concerning the disposal/regeneration of the spent ‘green’ nZVI sorbent must lead to new research in this field. Current large-scale immobilization techniques usually use gravitation separation and recirculation of nZVIs as a feasible process of applying nZVI for wastewater treatment; nZVI can be easily separated via gravitational settling and be recycled via pumping, and nZVI recirculation increases material efficiency and enriches the heavy metal contents in reacted nZVI (Li et al. 2014, 2016).

The usage of ‘green’ nZVIs for metal removal is still insufficiently researched. There have only been a few research papers which have shown that ‘green’ nZVI was efficient for metal removal from aqueous solutions. Desalegn et al. (2016) proved that mango peel nano-zero-valent iron was efficient for Cr(VI) reduction and our previous work confirmed that nZVIs produced by oak, mulberry and cherry leaf extracts can remove As(III) and Cr(VI) from aqueous solutions (Poguberović et al. 2016).

The present study focuses on the following objectives: (1) synthesis of the nZVI by using polyphenols from oak and mulberry leaf extracts; (2) determination of adsorption kinetic parameters for Ni(II) and Cu(II) on green nZVIs; (3) obtaining adsorption isotherms of Ni(II) and Cu(II) on green nZVIs; and (4) evaluation of the pH effect on Ni(II) and Cu(II) removal efficiency.

MATERIALS AND METHODS

Preparation of ‘green’ zero-valent iron nanoparticles

The oak and mulberry leaves were chosen because of their high antioxidant capacity as an important property for the production of the nZVIs. Also, oak and mulberry trees are widely distributed and abundant in Vojvodina, the northern province of Serbia. Oak leaves were collected from oak trees (Quercus petraea) growing in the National Park of Fruska Gora in northern Srem and mulberry leaves were collected from Morus alba trees, which grow in the gardens in north Srem, Vojvodina, Serbia. Collected leaves were milled using a normal kitchen chopper and sieved using a 2 mm sieve. Material with size below 2 mm was pre-dried at 50 °C in an oven for 48 h. Thus the prepared leaves were used for extraction and production of zero-valent iron nanoparticles.

The extraction procedure was carried out completely as according to Machado et al. (2015). An amount of 5.7 g of leaf was weighed and transferred to a 300 mL Erlenmeyer flask, to which 100 mL of water was added. The flask was then placed in a shaker bath, at 80 °C for 20 min for the flask with oak leaves, and at 80 °C for 60 min for the flask with mulberry leaves. After shaking, the solution was filtered with a Buchner vacuum filtration funnel and the filtrate was used for ‘green’ nZVI production. The extract of the leaves was mixed with 0.1 M Fe(III) solution in a volume ratio of 3:1 and the Fe(0) weight was 0.0014 gFe(0)/mL. The pH values of the leaf extracts before mixing with 0.1M Fe(III) were 1.9 for oak and 2.5 for mulberry, and after adding Fe(III) pH values were 2.1 for OL-nZVI and 2.8 for ML-nZVI.

In our previous work (Poguberović et al. 2016) transmission electron microscopy (TEM; Philips CM 10) and scanning electron microscope analyses (SEM; Hitachi S-4700 Type II) were used to determine morphology, size and nZVI particle distribution. For SEM images, powdered samples were first affixed onto adhesive tapes supported on metallic discs and then covered with a thin, electrically...
Conductive gold film. Images were recorded at different magnifications at an operating voltage of 50 kV.

Adsorption experiments

The stock solutions of Ni(II) and Cu(II) were prepared by dissolving appropriate amounts of NiSO₄·6H₂O and CuSO₄·5H₂O, into deionized water. Working solutions fi

10 mg/L in a final reaction mixture volume of 50 mL. Working solutions were prepared with deionized water to the desired concentrations. The chosen concentrations of Ni(II) and Cu(II) in aqueous solutions were in a wide range (1–250 mg/L) so they could represent pollution of groundwater or wastewater.

In order to investigate adsorption of Ni(II) and Cu(II) on OL-nZVI and ML-nZVI in aqueous solution, batch experiments were carried out under laboratory conditions, at room temperature (23 ± 1 °C), on a rotary shaker with 150 rpm. Batch experiments were applied on every sample in triplicate and the RSDs were below 5%.

For the adsorption kinetics study, the dosage of the OL-nZVI and ML-nZVI was held constant at 2 mL, and initial concentrations of Ni(II) and Cu(II) were 10 mg/L in a final reaction mixture volume of 50 mL. The initial pH values of the solutions were 2.5 for OL-nZVI mixtures and 4.0 for ML-nZVI mixtures; pH correction was not performed. Reactions were stopped in the following reaction intervals: 5, 10, 20, 30, 45, 60 and 80 min.

A pseudo-first-order kinetics model and pseudo-second-order kinetics model were employed in order to describe the adsorption rate. The pseudo-first-order kinetic model can be written as follows:

\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]

where \( q_e \) and \( q_t \) are the amount of Ni(II) or Cu(II) adsorbed (mg/g) on OL-nZVI and ML-nZVI at equilibrium and at time \( t \) (min) and \( k_1 \) represents the pseudo-first-order rate constant (g/mg min). For practical use in the analysis of kinetic parameters, Equation (1) is converted to the linear form:

\[
\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303}
\]

The pseudo-first-order rate constant \( k_1 \) was obtained from the curve \( \log(q_e - q_t) \) vs \( t \). Equation (3) represents the pseudo-second-order rate equation and can be written as follows:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \( k_2 \) is the pseudo-second-order rate constant (g/mg min). The linear form of Equation (3) was obtained.

Adsorption isotherms were obtained by adding 2 mL of ‘green’ nZVI to aqueous solutions with different initial Ni(II) and Cu(II) concentrations in the range of 1–250 mg/L. The final volume of all reaction mixtures was 50 mL. The reaction time was 60 min at an initial solution pH of 2.5 for OL-nZVI mixture and 4.0 for ML-nZVI.

Adsorption isotherms can explain the relationship between adsorbate and adsorbent and can provide the parameters for designing a desired adsorption model. Langmuir and Freundlich adsorption models were used to describe Ni(II) and Cu(II) adsorption on OL-nZVI and ML-nZVI. While the Langmuir model assumes monolayer adsorption with a finite number of identical sites, the Freundlich model is empirical in nature and allows multilayer adsorption (Bhowmick et al. 2014). The Langmuir and Freundlich models can be expressed as:

\[
\frac{C_e}{q_e} = \left( \frac{C_e}{q_m} \right) + \left( \frac{1}{K_L q_m} \right)
\]

\[
\log q_m = \log K_f + \left( \frac{1}{n} \right) \log C_e
\]

where \( q_m \) is the monolayer maximum adsorption capacity (mg/g), \( K_L \) is the Langmuir constant related to the energy of adsorption and \( K_f \) and \( 1/n \) are the Freundlich constant related to adsorption capacity and adsorption intensity respectively, and \( C_e \) is the equilibrium concentration of Ni(II) and Cu(II) in the liquid phase (mg/g).

The influence of initial pH value on adsorption was studied on 25 mg/L of Ni(II) and Cu(II) solutions mixed with 2 mL of ‘green’ nZVI in a final reaction mixture volume of 50 mL in pH range 2.5–10. The pH was adjusted using 0.1 M NaOH and 0.1 M HNO₃ solutions after the addition of ‘green’ nZVI in the solutions and was measured by the pH electrode.

Reaction between ‘green’ nZVI and the metals resulted in a black precipitate and then reaction mixtures were centrifuged for 12 minutes at 4,000 rpm and filtered using a hydrophilic PES 0.22 μm filter (Millipore Millex-GP) to separate the solid particles and solution. Residual concentrations of Ni(II) and Cu(II) in the filtrates were
determined by atomic adsorption spectrometry (AAS; Perkin Elmer AAnalyst™ 700).

The uptake amounts of Ni(II) and Cu(II) by OL-nZVI and ML-nZVI were calculated from the following formula:

\[ q_e = \frac{(C_0 - C_e) V}{m} \tag{6} \]

where \( q_e \) is the uptake of Ni(II) or Cu(II) onto the OL-nZVI and ML-nZVI, \( C_0 \) is the initial concentration of Ni(II) or Cu(II) (mg/L), \( C_e \) is the equilibrium concentration of Ni(II) or Cu(II) (mg/L), \( V \) is the volume of solution (mL), and \( m \) is the weight of the ‘green’ adsorbent (g). The specific weight of the aqueous ‘green’ adsorbent was 0.0014 gFe(0)/mL.

RESULTS AND DISCUSSION

Characterization

Characterization of the produced green nZVI materials (OL-nZVI and ML-nZVI) reported in our previous work (Poguberović et al. 2016) confirmed the formation of nano-size zero-valent iron particles within the size range of 10–50 nm. The TEM and SEM images showed that nanoparticles were spherical in shape and represented stable material with minimum agglomeration.

Adsorption kinetics

The adsorption kinetic parameters for Ni(II) and Cu(II) on OL-nZVI and ML-nZVI are presented in Figure 1, which shows that the equilibrium time was found within 10 and 45 min, respectively. The adsorption process was rapid within the first 5 min. After that reaction time, the adsorbed amounts of Ni(II) and Cu(II) on OL-nZVI remained nearly constant, while the adsorbed amount of metals on ML-nZVI slightly decreased after 45 minutes and remained constant. Better removal of Cu(II) than Ni(II) can be explained through the more positive redox potential of Cu(II) than Ni(II), which involves, beside adsorption and reduction and precipitation, other metal–nZVI interactions such as oxidation and co-precipitation of Cu(II) depending upon the prevailing geochemical conditions, such as pH, Eh and initial concentration and speciation of metals (O’Carroll et al. 2013), while Ni(II) may be removed by nZVI via reduction to Ni(0) and by adsorption as Ni(II) (Efecan et al. 2009; O’Carroll et al. 2013).

To evaluate the kinetics of the adsorption process, the first- and second-order kinetic models were tested to interpret the experimental data. Figures 2(c) and 2(d) show the plots of \( t/q_t \) vs \( t \) for Ni(II) and Cu(II) and the values of \( k_1 \) and \( k_2 \) calculated from the slopes and intercepts of the curves (Table 1). From the calculated (cal) parameters (Table 1) it can be seen that the pseudo-second-order kinetic model is a better fit to the experimental (exp) data than the pseudo-first-order kinetic model, and the coefficients of determination \( R^2 \) are higher than for the pseudo-first-order kinetic model. The value of \( q_e \) (cal) is approximately the same as \( q_e \) (exp) for both metals. The results of the adsorption kinetics indicate that Ni(II) and Cu(II) uptake on OL-nZVI and ML-nZVI follows the pseudo-second-order kinetic model, as numerous studies have shown (Demirbas et al. 2009; Feng et al. 2009; Kumar et al. 2011; Komy et al. 2014; Xia et al. 2014; Kyzas et al. 2015; Mangaleshwaran et al. 2015).

Adsorption isotherms

The initial metal concentration in the liquid phase significantly affects the adsorption process. At low initial metal concentrations the ratio of metal cations to adsorbent mass is low and thus adsorption does not depend on initial concentration (Malamis & Katsou 2013). Ni(II) is initially bound to the nZVI surface by physical sorption, then binds strongly by chemisorptions and is finally reduced to Ni(0) (Li & Zhang 2006). Cu(II) may be transferred via chemical reduction to its elemental form and can be reduced to Cu+ by nZVI, resulting in the formation of Cu2O (O’Carroll et al. 2013). Increasing the initial concentration means that more metals are available and thus, more metal ions are adsorbed for constant adsorbent mass, which is confirmed by the adsorption isotherm results (Figure 3). From Figure 3 it can be seen that the maximum
adsorption capacity of both OL-nZVI and ML-nZVI was achieved when the initial metal concentration was highest. The capacity of the OL-nZVI was higher for Ni(II) and the maximum adsorption capacity was found to be 777.3 mg Ni/g, while the ML-nZVI capacity was higher for Cu(II) adsorption and was found to be 1,047 mg Cu/g. These results are much higher than the adsorption capacities reported for nZVI (Ni(II): about 80 mg/g, Cu(II): 250 mg/g) (Karabelli et al. 2013; Efecan et al. 2013) and other low-cost materials: pecan shell carbon (Cu(II): 95.0 mg/g) (Shawabkeh et al. 2013), hazelnut shell activated carbon (Cu(II): 58.67 mg/g) (Demirbas et al. 2009), cashew nut shell (Ni(II): 10.892 mg/g) (Kumar et al. 2011), nettle ash (Ni(II): 192.3 mg/g) (Mousavi & Seyed 2011), hemp biomaterials

![Figure 2](image1.png)

**Figure 2** | The pseudo-first-order (a), (b) and pseudo-second-order (c), (d) kinetic model data for Ni(II) and Cu(II).

<table>
<thead>
<tr>
<th>Exp</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$, exp</td>
<td>$k_1$, $q_{cal}$</td>
</tr>
<tr>
<td>Ni/OL-nZVI</td>
<td>30.88</td>
<td>0.279</td>
</tr>
<tr>
<td>Ni/ML-nZVI</td>
<td>57.17</td>
<td>0.0239</td>
</tr>
<tr>
<td>Cu/OL-nZVI</td>
<td>71.31</td>
<td>0.0442</td>
</tr>
<tr>
<td>Cu/ML-nZVI</td>
<td>74.91</td>
<td>0.0350</td>
</tr>
</tbody>
</table>

![Figure 3](image2.png)

**Figure 3** | Adsorption isotherm parameters for the adsorption of Ni(II) and Cu(II) on the OL-nZVI and ML-nZVI.
(Ni(II): about 120 to 150 mg/g) (Kyzas et al. 2015) and cotton seed cake (Cu(II): 289 mg/g) (Thirugnanasambandham & Sivakumar 2015). The much higher adsorption capacities of OL-nZVI and ML-nZVI than other tested materials may be related to the much smaller particle size which is indicative of a larger specific surface area that can offer more reactive sites, higher reactivity and better dispersion (Li et al. 2012).

The adsorption data for OL-nZVI and ML-nZVI was fitted to Langmuir and Freundlich models (Figure 4) and the relative parameters calculated from the two models are listed in Table 2. The correlation coefficients indicate that the adsorption data are better fitted by the Freundlich model ($R^2 > 0.99$) than the Langmuir model for Ni(II) and Cu(II) on ML-nZVI. While correlation coefficients for Cu(II) adsorption on OL-nZVI indicate that the adsorption data are better fitted by the Langmuir model ($R^2 > 0.993$) than the Freundlich model ($R^2 > 0.981$), which means that the adsorption involved the formation of a monolayer on a homogenous surface. The values of $1/n$ were lower than 1, thus signifying favorable adsorption of Ni(II) and Cu(II) on green nZVIs. It can be found from Table 2 that the calculated maximum adsorption capacities obtained for OL-nZVI and ML-nZVI with Ni(II) and Cu(II) were higher than the

| Adsorption data from Langmuir and Freundlich adsorption models for the adsorption of Ni(II) and Cu(II) on the OL-nZVI and ML-nZVI |
|-----------------|-----------------|-----------|-----------|-------|-------|-------|-------|
| Langmuir        | Freundlich      | q<sub>m</sub> (mg/g) | K<sub>L</sub> (L/mg) | R<sub>L</sub> | R<sup>2</sup> | 1/n | K<sub>f</sub> (l/g) | R<sup>2</sup> |
| Ni/OL-nZVI      |                 | 1,159     | 0.0110  | 0.994–0.305 | 0.983 | 0.782 | 0.0110 | 15.91 | 0.995 |
| Ni/ML-nZVI      |                 | 639.5     | 0.0142  | 0.986–0.220 | 0.963 | 0.683 | 0.0142 | 15.23 | 0.997 |
| Cu/OL-nZVI      |                 | 452.5     | 0.0360  | 0.965–0.100 | 0.993 | 0.591 | 0.0360 | 22.32 | 0.981 |
| Cu/ML-nZVI      |                 | 1,388     | 0.00169 | 0.998–0.703 | 0.987 | 0.722 | 0.00169 | 1.482 | 0.996 |

Figure 4 | Langmuir (a, b) and Freundlich (c, d) adsorption isotherms of Ni(II) and Cu(II) on OL-nZVI and ML-nZVI.
maximum adsorption capacities achieved during the experiment for both green nZVI. Kumar et al. (2011) reported results for Ni(II) adsorption on cashew nut shell indicating that the adsorption data fitted well with both models, while Mousavi & Seyedi (2011), Feng et al. (2009), Demirbas et al. (2009), and Thirugnanasambandham & Sivakumar (2015) reported that Ni(II) and Cu(II) adsorptions on nettle ash, modified orange peel, hazelnut shell activated carbon, and cotton seed cake are better fitted by the Langmuir than the Freundlich model.

**Effect of initial pH**

Solution pH can have a significant influence on the adsorption of heavy metals, due to the metal sorption, surface charge and functional group chemistry of the adsorbent (Kim et al. 2013).

Hence, 2 mL of green nZVI was mixed with solutions containing 25 mg/L Ni(II) or Cu(II) at an initial pH of 2.5–10 (23 ± 1°C). The pH of the solutions was 2.5 after adding OL-nZVI, and 4.0 after adding ML-nZVI. The pH of the solutions was adjusted after the ‘green’ nZVI addition. Varying the initial pH had a great effect on Ni(II) and Cu(II) removal (Figure 5). As Figure 5 shows, adsorbed amounts of Ni(II) and Cu(II) increased with the pH increase to pH 7.0 and 8.0. When pH was 8.0 the Ni(II) uptake was 413.4 mg/g OL-nZVI and 251.1 mg/g ML-nZVI and when pH was 7.0 the Cu(II) uptake was 411.7 mg/g OL-nZVI and 229.2 mg/g ML-nZVI, which is consistent with previous literature where similar pH-dependent Ni(II) and Cu(II) adsorption on other adsorbents has been documented (Demirbas et al. 2009; Efecan et al. 2009; Feng et al. 2009; Kumar et al. 2011; Malamis & Katsou 2013; Komy et al. 2014; Thirugnanasambandham & Sivakumar 2015). This behavior refers to the competition of H+ with Ni(II) and Cu(II) in a lower pH medium (pH = 7.0 and 8.0) for the available sorption sites of the adsorbate (Jiang et al. 2010; Komy et al. 2014). In addition, at lower pH, pH above pH<sub>PZC</sub>, OL-nZVI and ML-nZVI surfaces become positively charged, and thus electrostatic repulsion will occur between the surface sites and the Ni and Cu ions. The point of zero charge of the material was experimentally determined in our previous work (Poguberović et al. 2016), and pH<sub>PZC</sub> was determined to be pH 2.4 for OL-nZVI and 3.8 for ML-nZVI. In contrast, at high pH, OH− ions present in the aqueous solution will compete with Ni(II) and Cu(II) for adsorption sites. The pH strongly influences the redox reactions occurring at the ZVI surface by accelerating corrosion at low pH and passivating the iron surface at high pH through the formation of iron (hydr)oxides (O’Carroll et al. 2013). The impact of pH on metal removal by nZVI depends on the oxidation state of the metal and the removal mechanism. Passivation of the nZVI surface at high pH hinders electron transfer from the Fe(0) core, thus decreasing the removal of metal contaminants by reductive precipitation. The strong decrease in adsorption that was observed for Cu/OL-nZVI at high pH can be explained by the fact that high pH decreases adsorption of metal anions due to electrostatic repulsion caused by the negative nZVI surface charge above a pH of 7.8. However, even when the pH reached higher than 7.0 and 8.0, the green nZVIs still showed greater metal uptake as opposed to when the pH was 2.5. So, the adsorption capacity of ‘green’ nZVIs for Ni(II) and Cu(II) is optimal in the pH range from 7.0 to 8.0. This indicates that the reduction of Ni(II) and Cu(II) by ‘green’ nZVIs is strongly pH-dependent and that synthesized ‘green’ nZVIs are superior for the removal of Ni(II) and Cu(II) at the pH of most groundwaters. More research is needed to study the effect of pH on metal removal by nZVI to determine the specific impact on each removal mechanism.

**CONCLUSIONS**

Oak and mulberry leaf extracts were used to prepare ‘green’ nZVI adsorbents and to remove Ni(II) and Cu(II) from aqueous solution. Kinetics studies showed that ‘green’ nZVIs are effective in the removal of both Ni(II) and Cu(II) with fast kinetics and a rate of adsorption that follows pseudo-second order. The adsorption isotherm results show that the capacity of the OL-nZVI is higher for Ni(II) and was found to be 777.3 mg Ni/g, while the ML-nZVI capacity is higher.
for Cu(II) adsorption and was found to be 1,047 mgCu/g. The maximum removal of Ni(II) by ‘green’ nZVI is at pH = 8.0, while the maximum removal of Cu(II) is at pH = 7.0. Thus we hypothesize that the nZVIs produced by oak and mulberry leaf extracts reported in this paper are relevant for preparing environmentally friendly, non-toxic and low-cost adsorbents to remediate Ni(II) and Cu(II) from aqueous solutions. For full-scale applications of ‘green’ nanotechnology in water/wastewater treatment, separation of spent ‘green’ nZVI must be further investigated. The low cost of ‘green’ nZVIs (OL-nZVI and ML-nZVI) is reflected in the preparation of those materials. First, oak, and mulberry trees are abundant and easy to find in Vojvodina, the northern province of Serbia, and fallen leaves can be used for nZVI preparation. In addition, the price of the Fe(III) solution used (FeCl₃·6H₂O) is much lower in comparison with all chemicals used in the conventional (sodium borohydride) method.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project Nos III43005 and TR37004).

REFERENCES


First received 23 September 2015; accepted in revised form 4 August 2016. Available online 13 August 2016