

# Biosorption of $\text{Cu}^{2+}$ and $\text{Ni}^{2+}$ ions from aqueous solutions using waste dried activated sludge biomass

Sukru Aslan<sup>\*1</sup>, Sayiter Yildiz<sup>1</sup>, Mustafa Ozturk<sup>2</sup>

<sup>1</sup>Department of Environmental Engineering, Sivas Cumhuriyet University, 58140, Sivas, Turkey

<sup>2</sup>Department of Organic Agriculture, Sivas Vocational School of Higher Education, Sivas Cumhuriyet University, 58140, Sivas, Turkey

\*Corresponding author: e-mail: saslan@cumhuriyet.edu.tr

Adsorption of Cu(II) and Ni(II) ions onto the waste powdered activated sludge biomass (PWB), which was obtained from the biological wastewater treatment plant, was investigated in this experimental study. The effects of contact time, pH, temperature, initial sorbate and sorbent concentrations on the adsorption were determined. The BET surface area, pore volume, and pore diameter of PWB were found to be about 0.51 m<sup>2</sup>/g, 0.0053 cm<sup>3</sup>/g, and 41.4 nm, respectively. Considering the R<sup>2</sup> value, q<sub>exp</sub> and q<sub>cal</sub>, the Langmuir and Freundlich models were well described for Cu(II) and Ni(II) adsorption, respectively. The adsorption mechanism of Cu(II) and Ni(II) onto the PWB could be better simulated by the pseudo-second-order kinetic mechanism than the pseudo-first-order, intra particle diffusion and Elovich models. Thermodynamic aspects of the adsorption of heavy metals were also investigated. Considering the applied desorbing agents for reuse of PWB for Ni(II) recovery, desorption cycle is not feasible due to the deterioration of the PWB structure.

**Keywords:** adsorption, copper, nickel, waste biomass.

## INTRODUCTION

Most of the industrial wastewaters contain one or more heavy metals. Due to the toxicity of heavy metals to humans and aquatic life, industrial wastewaters have been causing a growing concern since 1970s<sup>1</sup>. Industrial processes, such as mining, electroplating, textile, fertilizer production, battery manufacturing, metallurgy, electronics, tanneries, etc. discharge wastewater contaminated with various heavy metals, which cause a serious environmental problem. Copper and nickel are the most common heavy metals in the industrial wastewater<sup>2</sup>. Although various water and wastewater treatment processes such as chemical precipitation, electro coagulation, membrane separation, ion exchange etc. have been applied to remove heavy metals, adsorption is considered attractive method due to the cost and efficiency<sup>3, 4</sup>.

As an environment-friendly and cost-effective material, biowaste materials have been widely applied to remove heavy metals from aqueous solution. In last two decades, various types of waste biosorbents, such as an activated sludge<sup>1, 5–11</sup>, digested sludge<sup>12, 13</sup>, algae<sup>14</sup>, fungi<sup>15, 16</sup>, and others have been successfully used for treating various metal ions in the solution.

Mixed liquor suspended solids called activated sludge contains wide variety of microorganisms (bacteria and protozoa) in the biological reactor of a wastewater treatment plant (WWTP). The organic and inorganic pollutants in wastewaters are converted by the microorganisms to the end products (CO<sub>2</sub>, N<sub>2</sub> etc.) and new biomass in the biological WWTP. Waste biosludge contain about 1–2% biomass is transferred to the sludge treatment units. Excessive amount (about 45 million/years) of biological dry solids is produced in the world<sup>17</sup>. Due to the treatment (aerobic or anaerobic digestion) and disposal (incineration and landfill site deposition) cost of biosludge, its management is one of the most important problems in the world<sup>18, 19</sup>. The dried dead waste biosludge has a large specific surface area which is used for the adsorption of pollutants from waters<sup>20</sup>.

Because the waste dried sludge has been considered as a competitive, effective, and cheap adsorbent<sup>21</sup>, it has been widely used for adsorption of heavy metals for water treatments in recent years<sup>1, 8, 21–27</sup>.

Most of the bacteria have cell wall which consists of carboxyl, acidic polysaccharides, amino acids and other components<sup>8</sup>. Biosorption of heavy metal ions onto the biomass surface is attributed to negatively charged functional groups of the extracellular polymeric substances (EPS) which makes the formation of complexes with heavy metals<sup>8, 10, 28, 29</sup>.

Acclimation and stimulation of biomass by special nutrients enhance the biosorption of heavy metals in the aqueous solution<sup>30</sup>. The biosorption capacity of activated sludge depends on the metal species and C/N ratio in the growth medium which changes the composition of EPS<sup>10, 30, 31</sup>.

The enormous amount of waste biomass is produced in a biological WWTP and its disposal is one of the most important environmental problems in the world. The aim of present study is to investigate the reusability and capacity of dried sludge to adsorb the heavy metals Cu(II) and Ni(II). Additionally, release of the organic and nitrogen compounds from the biomass under various experimental conditions were investigated. In this experimental study, the adsorption capacity of Cu(II) and Ni(II) ions onto powdered waste biomass (PWB) were investigated under various conditions (pH, temperature, initial heavy metal concentrations, and mixing time). The biosorption capacity and adsorption rates of PWB were evaluated by applying isotherm and kinetic models, respectively. Thermodynamic parameters enthalpy ( $\Delta H^\circ$ ), free energy ( $\Delta G^\circ$ ) and entropy ( $\Delta S^\circ$ ) changes were also determined. Recovery of Ni(II) ions by using various desorbing agents was studied to evaluate the reusability of waste biomass.

## MATERIAL AND METHODS

### Sivas municipal wastewater treatment plant

Sivas WWTP consists of mechanical units (screening and grit removal) and biological units (anaerobic, aerobic and anoxic stage). Biological removal of organics, nitrogen compounds ( $\text{NH}_4\text{-N}$  and  $\text{NO}_x\text{-N}$ ) and phosphorous in the wastewaters are carried out by autotrophic and heterotrophic microorganisms in the suspended-growth reactors.

### Biosorbent preparation

Waste biomass was withdrawn from the settling tank of Sivas WWTP. In order to remove impurities, the sludge was washed with tap and distilled waters several times and dried at about  $60^\circ\text{C}$  for 48 hours. Dried biomass was grounded into small pieces in a mortar to powder and sieved to constant sizes (250  $\mu\text{m}$ ) and stored in the plastic bottles for experimental studies.

### Adsorption/Desorption experiments

100 mg PWB were mixed with 100 mL of the Cu(II) and Ni(II) solutions in an Erlenmeyer flask. Stock solutions of 1000 mg/L Cu(II) and Ni(II) were prepared using analytical reagent grades of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , respectively. All solutions were prepared by using the distilled water. The initial pH of solution was adjusted to the desired value by addition of 0.1 N  $\text{H}_2\text{SO}_4$  or 0.1 NaOH solutions. After determining the equilibrium time for batch experiments, the final pH of solution was also measured.

Batch adsorption experiments were carried out using an orbital incubator shaker (Gerhardt) at 125 rpm. After completing the experiments, the obtained solutions with residual Cu(II) and Ni(II) were separated from the PWB prior to analysis by centrifugation at 3000 rpm/min for 10 minutes (NF800, NUVE). A control flask free of PWB with 25 mg/L Cu(II) and Ni(II) were used to obtain the extent of non-adsorptive Cu(II) and Ni(II) removal from aqueous solution.

Batch adsorption experiments under various conditions (pH 3.0–6.0 for Cu(II), pH 3.0–7.0 for Ni(II) and the temperature of  $20\text{--}55^\circ\text{C}$ ) were performed to investigate the adsorption characteristics of PWB.

The constants of adsorption isotherm were determined with the initial Cu(II)/Ni(II) and PWB concentrations varying from 5 to 50 mg/L and from 0.25 to 2.0 mg/L, respectively.

In order to test the reusability of PWB, sorption-desorption-sorption of Ni(II) cycles were performed. For the desorption study, 1.0 g of PWB was firstly exposed to 250 mg/L Ni(II) at a ratio of sorbent to volume of solution of 1:100 at  $25^\circ\text{C}$  and 125 rpm for 120 min. After the sorption experiment, the PWB was collected by centrifugation and washed at least two times with distilled water and dried at  $105^\circ\text{C}$  for 24 hours. Secondly, 0.1 g of the PWB residue was reloaded with 25 mg Ni(II)/L.

Desorption experiments were carried out with Ni(II) coated PWB by using desorption agent including 0.1 M  $\text{H}_2\text{SO}_4$ , 0.1 M HCl at the pH of about 1.0 and distilled water at a pH value about 5.5.

Recovered 0.1 g of the PWB was transferred to the 100 mL desorption solutions. The aqueous solutions were

shaken for the defined equilibrium time for Ni(II) then the samples were analysed to determine the concentration of sorbate after desorption. The recovery percent of desorption is calculated by Eq1.

$$(\%) \text{ Recovery} = \frac{\text{amount of Ni(II) ions desorbed}}{\text{amount of Ni(II) ions biosorbed}} \times 100 \quad (1)$$

In order to determine the adsorption capacity differences between unused and used PWB, adsorption experiments were repeated with used PWB after desorption experiments.

Reversibility of the Ni(II) adsorption process by measuring Ni(II) desorption from the PWB was determined.

### Analytical methods

Concentrations of Cu(II), Ni(II) and  $\text{NH}_4\text{-N}$  in the clear samples were determined by the analytical kits of Cu(II) (code no: 14785), Ni(II) (code no: 14767), and  $\text{NH}_4\text{-N}$  (code no: 14752) using a spectrophotometer (Merck, PHARO100). Concentrations of organic matter released from the PWB were determined as the chemical oxygen demand (COD) analysis<sup>32</sup> in the samples.

The adsorbent characterization was carried out by SEM, BET, EDX, and FT-IR were determined in the laboratory of Kayseri Teknokent.

In order to be sure that the adsorption is performed just with the PWB, batch experiments were performed simultaneously in triplicate with the controls (without PWB). After reaching the equilibrium, the filtrate in the batch unit was analysed for determining the final concentrations of heavy metals. The removal efficiency ( $E$ , %) and sorption capacity ( $q_e$ , mg/g) of metal ions were calculated by means of subsequent equation (2) and (3), respectively.

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

$$E = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3)$$

Where,  $C_0$  and  $C_e$  (mg/L): initial and final concentrations of heavy metals,  $V$  (L): solution volume,  $m$  (g): mass of the sorbent.

### Results and discussion

The data which are presented in tables and figures are the mean value (standard deviation  $\leq 5\%$ ). Variations of the pH levels between initial and final solutions were negligible throughout the experimental studies.

### Characterization of PWB

In order to determine the surface structure and morphology of PWB, the scanning electron microscopy analysis was carried out. As can be seen in Fig 1, PWB has considerable numbers of pores for adsorption. The BET surface area, pore volume, and pore diameter of PWB were about  $0.51 \text{ m}^2/\text{g}$ ,  $0.0053 \text{ cm}^3/\text{g}$ , and 41.4 nm, respectively. The chemical composition of PWB was determined by using EDX analysis (Fig. 2). The results indicated that the dominant peak was  $\text{SiO}_2$  crystals (quartz) which was consistent with the literature<sup>33–35</sup>. Other

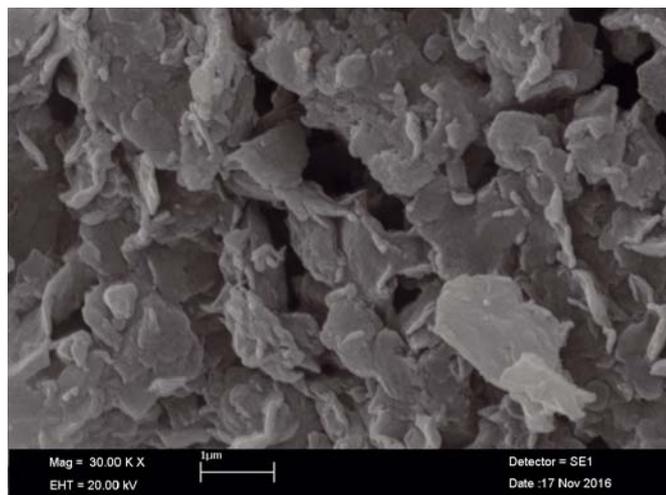


Figure 1. SEM images of raw PWB

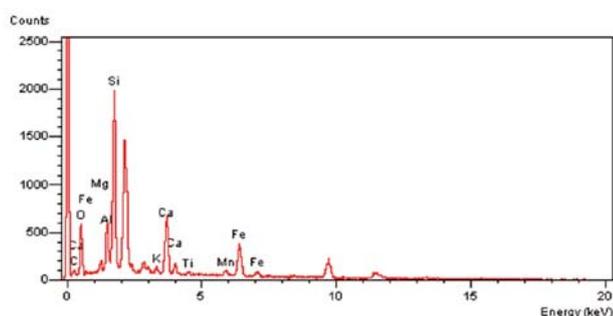
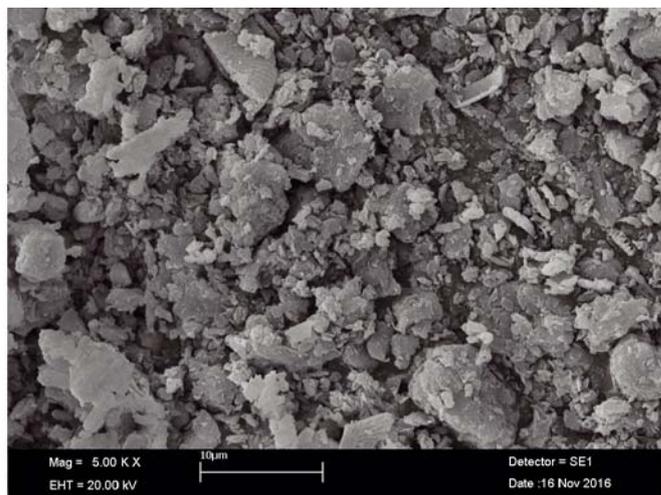


Figure 2. The EDX patterns of raw PWB

characteristic peaks show the presence of Ca, Al, Fe, Mg, C, Mn, and K.

The absorbance spectrum of raw PWB was shown in Fig 3. In the FT-IR spectrum, the adsorption bands at  $3270\text{ cm}^{-1}$  could be attributed to the C-H and N-H stretching vibration. The bands at  $2956$ ,  $2918$ , and  $2849\text{ cm}^{-1}$  were assigned to the C-H stretching mode indicating material of the aliphatic nature<sup>1, 36-38</sup>. The data at about  $1633\text{ cm}^{-1}$  and  $1538\text{ cm}^{-1}$  indicated to asymmetric and symmetric stretching of carboxylate, respectively<sup>1</sup>. The peak at  $1410\text{ cm}^{-1}$  could be attributed to the symmetric stretching of COO-group<sup>39</sup>. The peak at  $1037\text{ cm}^{-1}$  along with the peak at  $1241\text{ cm}^{-1}$  could be attributed to C-O and C-N stretching vibration<sup>1</sup> and protein fractions<sup>40</sup>. The fingerprint region between  $900$  and  $600\text{ cm}^{-1}$  exhibited ring vibrations from aromatic amino acids and nucleotids<sup>41</sup>. The peaks between  $897\text{ cm}^{-1}$  and  $999\text{ cm}^{-1}$  were attributed to the O-P-O stretching in nucleic acids by Yin *et al.*<sup>42</sup>. Because of the dominant peak for  $\text{SiO}_2$

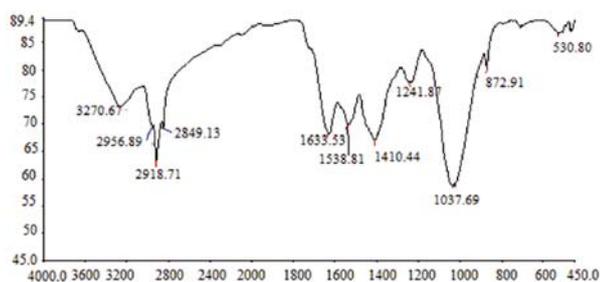


Figure 3. The FT-IR spectra of the PWB

was observed with the EDX analysis, the absorption bands at about  $872\text{ cm}^{-1}$  and  $530\text{ cm}^{-1}$  were attributed to Si-O stretching and Si-O bending indicating of the silica presence.

#### Effect of contact time

After the sorption reaction starts, both adsorption and desorption of Cu(II) and Ni(II) onto the PWB occur until equilibrium is reached. A series of biosorption experiment was performed to determine the equilibrium time at the initial heavy metal concentrations of  $25\text{ mg/L}$  (Fig. 4). Most of the Cu(II) and Ni(II) ions in the units were adsorbed by the PWB at the first reaction times of 15 min and 20 min, respectively. The initial faster transfer rate of heavy metals from the solution onto the PWB might be attributed to the huge available surface area of PWB and relatively high concentration gradient of heavy metals between adsorbent and adsorbate. Consequently, the transfer rates of Cu(II) and Ni(II) ions from the solutions to the PWB gradually decreased with the increase of contact time. The initial adsorption rate is fast when the surface reaction process occurred and then the adsorption rate gradually decreased due to the decrease of available site of the adsorbent<sup>3</sup>. For contact time up to 30 min, about 70% of Cu(II) and 43.5% of Ni(II) was removed from the aqueous phase. As can be seen from the Fig. 4, Cu(II) and Ni(II) ions adsorption onto the PWB increased with contact time up to 60 min and 120 min, respectively. However, to be sure of the best biosorption conditions, batch experiments were carried out for the contact times of 120 min and 360

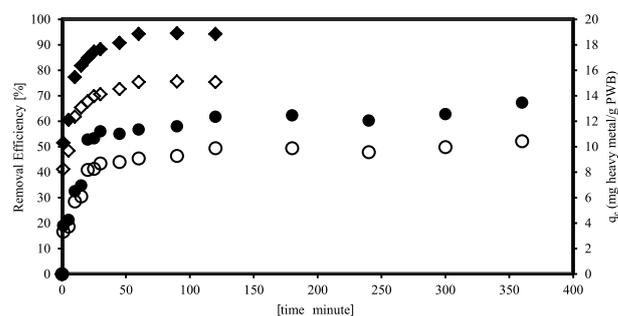


Figure 4. The effect of contact time on Cu(II) and Ni(II) removal by the PWB

min for Cu(II) and Ni(II), respectively. After reaching the equilibrium times, there were no considerable change in Cu(II) and Ni(II) ions removal. For Cu(II) and Ni(II), sorption rate reaches up to 18.9 mg/g and 13.5 mg/g when the contact time was 60 min and 120 min, respectively. About removal efficiencies of 75% Cu(II) and 52% Ni(II) was achieved at the equilibrium times.

Taking into account the results, contact time of 60 min and 120 min was chosen for further experiments for Cu(II) and Ni(II), respectively.

### Effect of initial pH

The extractability of heavy metal ions from the aqueous phase is pH dependent<sup>38</sup>. Since pH effect the surface charge of sorbent, the adsorbate ionization state, and form of adsorbate<sup>8, 43, 44</sup>, the pH of solution is one of the most important factors on the rate and the extent of adsorption<sup>8</sup>.

The adsorption capacity and removal efficiency of PWB for Cu(II) and Ni(II) ions as functions of pH are presented in Fig. 5. For Ni(II) biosorption, the adsorption capacity and removal efficiency increased slightly with rising the pH values. Bermudez *et al.*<sup>45</sup> reported that the nickel speciation is not changed by the pH variations, so the major effect on the adsorption might be attributed to the sorbent functional group which is affected by pH. The highest Ni(II) adsorption capacity and removal efficiency of 13.5 mg/g and 54% was determined at the initial pH of 7.0.

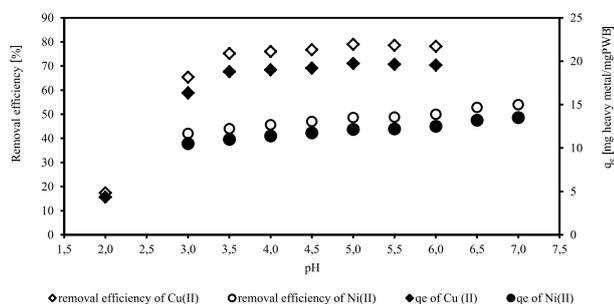


Figure 5. The effect of initial pH

Due to takes place the formation of precipitation form of copper, experiments were performed up to 6.0 of the solution initial pH value. Forms of Cu(OH)<sub>2</sub> takes places at pH higher than 5.0 and precipitate at the pH value greater than 6.0<sup>46</sup> consequently it promotes a reduction of the adsorption capacity.

On higher pH values, Cu(II) adsorption slightly decreased from 19.75 mg/g to 19.55 mg/g. The adsorption capacity and removal efficiency of Cu(II) ions increased sharply from 5.35 mg/g to 16.4 mg/g and from 17.4% to 65.4% with rising initial pH value from 2.0 to 3.0, respectively. However, the capacities of adsorption were slightly elevated with increasing the pH value when the pHs were between 3.0 and 6.0.

An increase in pH corresponded to an increase in biosorption while Cu(II) and Ni(II) biosorption reached the maximum capacity at the pH values of 5.0 and 7.0, respectively.

The COD and NH<sub>4</sub>-N concentrations at various pH were determined in the decant of batch units. Average concentrations of COD and NH<sub>4</sub>-N were about 173 mg/L

and 2.9 mg/L, respectively. Release of organic matter and NH<sub>4</sub>-N from the nitrification organism into the solution was also mentioned by Aslan and Topcu<sup>47</sup>.

### Effects of initial heavy metal concentrations

The adsorption capacity of PWB was determined for the initial Cu(II) and Ni(II) concentrations in the range of 5 mg/L-50 mg/L (Fig. 6). The adsorption capacity increased with increasing the initial heavy metal concentrations. Because the fractional adsorption is dependent on the initial heavy metal concentrations<sup>3</sup>, the lower adsorption at higher concentration of heavy metals resulted from an increased ratio of initial number of moles adsorbate to the available surface area of PWB.

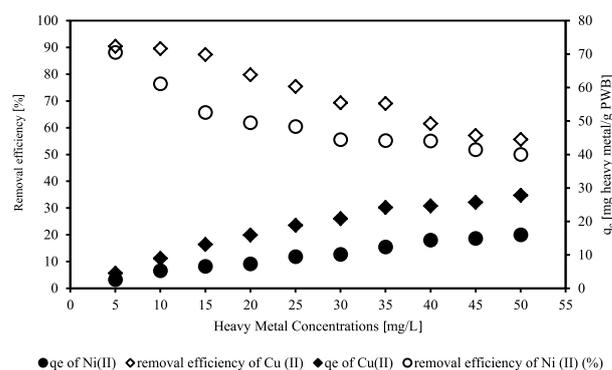


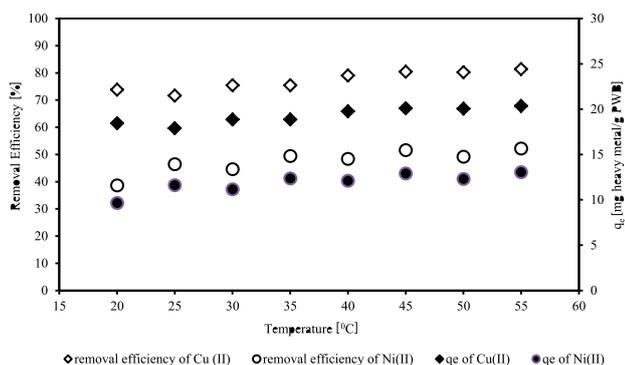
Figure 6. The effect of initial adsorbate concentrations

The results indicated that there was a reduction in adsorption, due to the lack of available sites required for the high initial heavy metal concentration. For the initial concentrations of 5 mg/L and 50 mg/L, the removal efficiencies of Cu(II) and Ni(II) decreased from about 90.4% to 55.6% and from 70.5% to 40%, respectively. When the heavy metal concentrations were low (5 mg/L), biosorption was limited by the Cu(II) and Ni(II) ion concentrations (yielding about 4.5 mg Cu(II)/g and 3.2 mg Ni(II)/g). However, at high concentrations (50 mg/L), the extent of biosorption was limited by the concentrations of the PWB yielding about 27.8 mg Cu(II) /g and 20 mg Ni(II)/g.

Katal *et al.*<sup>48</sup> reported that higher amount of pollutants were adsorbed at low concentrations because the PWB has more available surface area. The results are in agreement with the previous studies<sup>3, 8</sup>.

### Effects of temperature

The variations of  $q_e$  values and removal efficiencies are shown in Fig 7. Elevating the operational temperature from 20°C to 55°C provided the PWB to increase slightly its adsorption capacity for Cu(II) from about 18.5 mg/g to 20.4 mg/g and Ni(II) from about 9.7 mg/g to 13.1 mg/g. The maximum removal efficiency of Cu(II) (81.4%) and Ni(II) (52.2%) ion was observed at the temperature of 55°C. The sorption of Cu(II) and Ni(II) ions onto the PWB are endothermic, since the extent of both adsorption increased with elevating temperature. In addition to that, the adsorption capacity of heavy metals was increased due to the pores of PWB might be enlarged by high temperature<sup>49</sup>. However, the previous adsorption study indicated that the sorption capacity of biomass slightly

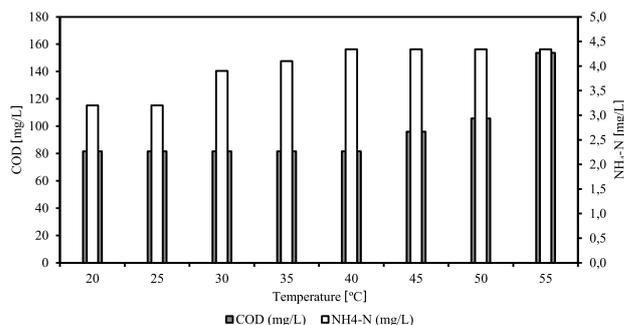


**Figure 7.** Temperature effect on the adsorption capacity of PWB

decreased when the temperature was higher than 60°C which might be denaturing of biomass wall structure<sup>11</sup>.

Experimental results suggested that the adsorption of heavy metals onto the PWB occurred chemically. Because of the collision frequency between PWB and heavy metals, increasing the temperature of aqueous solution, increased the kinetic energy of Cu(II) and Ni(II) particles and ions were electrostatically adsorbed to the PWB.

A chemical formula of microorganism is defined as C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>N contains different organic and inorganic compounds. When the biomass is exposed to the extreme conditions, some of compounds (organic matter, NH<sub>4</sub>-N, Ca<sup>2+</sup> and Mg<sup>2+</sup>) are released from the cell into the water<sup>5, 9, 24, 47</sup>. It was found that the concentrations of COD and NH<sub>4</sub>-N of water after adsorption increased with increasing temperature (Fig. 8). Elevating the temperature from 20 to 55°C, the release of COD (from



**Figure 8.** Temperature effect on the release of organic matter and NH<sub>4</sub>-N

81.6 mg/L to 153.6 mg/L) and NH<sub>4</sub>-N (from 3.2 mg/L to 4.34 mg/L) into the aqueous solution increased.

### Adsorption isotherms

Adsorption isotherm experiments were carried out in order to assess the heavy metal distribution between the aqueous phase and PWB. In order to describe the uptake of Cu(II) and Ni(II) ions by PWB, isotherm models (Table 1) were applied to test the experimental data of initial heavy metal and PWB concentrations.

By applying the models, constants  $q_m$  (monolayer sorption capacity, mg/g),  $b$  (mean free energy),  $E$  (sorption per molecule of sorbate),  $K_L$  (Langmuir constant, L/mg) and  $K_F$  (Freundlich constant, L/mg),  $q_{max}$  (maximum biosorption capacity, mg/g),  $b_T$  and  $A_T$  (Temkin parameters L/mg) were calculated. In the models,  $R$  (8.314 joule. mol/K) and  $T$  (K) are the universal gas constant and absolute temperature, respectively.

**Table 1.** Equation of Isotherms and kinetics<sup>50</sup>

	Equations	Plot	Parameters
<i>Equilibrium models</i>			
Langmuir	$q_e (mg/g) = q_m \frac{K_L C_e}{1 + K_L C_e}$ $R_L = 1/(1 + K_L \times C_0)$	$C_e/q_e$ vs. $C_e$	$q_m = 1/\text{slope}$ $k_L = \text{slope}/\text{intercept}$
Freundlich	$q_e (mg/g) = K_F C_e^{1/n}$	$\log q_e$ vs. $\log C_e$	$k_F = \exp(\text{intercept})$ $n = 1/(\text{slope})$
Temkin	$q_e (mg/g) = B \ln A_T + B \ln C_e$	$Q_e$ vs $\ln C_e$	$q_e = \text{slope}$ $A_T = \exp(\text{intercept})/(\text{slope})$
Dubinin-Radushkevich	$\ln q_e = \ln q_{max} - \beta \epsilon^2$ $\epsilon = RT \ln(1 + \frac{1}{C_e})$	$\ln q_e$ vs $\epsilon^2$	$q_0 = \exp(\text{intercept})$ $\beta = -(\text{slope})$
<i>Kinetic models</i>			
Pseudo first-order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$	$\log(q_e - q_t)$ vs $t$	$q_e = \exp(\text{intercept})$ $k_1 = -(\text{slope})$
Pseudo second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ $h = k_2 \times q_e^2$	$t/q_t$ vs $t$	$q_e = 1/(\text{slope})$ $k_2 = (\text{slope})^2/(\text{intercept})$
Intra particle diffusion	$q_t = k_{id} t^{1/2} + C$	$q_t$ vs $t^{1/2}$	$k_i = \text{slope}$
Elovich	$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t$	$q_t$ vs $\ln t$	$\beta = \text{slope}$ $\alpha = 1/(\text{slope}) \exp(\text{intercept}/\text{slope})$

The calculated constants and correlation coefficients of isotherms are summarized in Table 2 and 3. Maximum uptake ( $q_{\max}$ ) of the Cu(II) ions were obtained as 6.98 mg/g-8.8 mg/g by the Langmuir model parameters indicated that the monolayer saturation capacity of Cu(II).

The separation factor  $R_L$  was found to be lower than 1.0 (0.065-0.007,  $0 < R_L < 1$ ) for the initial concentrations between 5-50 mg Cu(II) /L. The value of  $R_L$  indicated that the adsorption of Cu(II) ion onto the PWB was favorable under the studied experimental conditions<sup>50,51</sup>.

As can be seen from the Table 2, regression correlation coefficient ( $R^2$ ) for the Ni(II)-PWB systems are high. The  $R^2$  and  $1/n$  values for the Freundlich model were 0.968 and 1.0, respectively. Model is suggesting the possible multilayer sorption and also Ni(II) sorption onto the PWB was unfavorable<sup>52</sup>. According to the Freundlich approach, uptake of adsorbate onto the adsorbent is increasing by increasing adsorbate concentrations in the solution<sup>53</sup>.

### Adsorption kinetics

In order to better design and operate the adsorption treatment unit, the kinetic of adsorption is very important to determine the pollutants removal rate<sup>54</sup>. In this study, adsorption kinetic models, Pseudo orders, Elovich, and intra particle diffusion were applied to test the experimental data of temperature (Table 1). The coefficients

and sorption capacity of experimental ( $q_{\text{exp}}$ ) and calculated ( $q_{\text{cal}}$ ) of kinetic models are listed in Table 4 and 5.

It was observed that the correlation coefficients of pseudo second order model are much higher than the values obtained from the other models. In addition, the  $q_{\text{e,cal}}$  values also agree very well with the  $q_{\text{e,exp}}$ . Results are suggesting that the Cu(II) and Ni(II) adsorption mechanism onto the PWB could be better simulated by the pseudo second order kinetic. The rate of adsorption process is controlled by the chemical interactions between functional groups of PWB and metal ions<sup>45</sup>.

### Thermodynamic parameters

The variations of sorption with temperature from 20°C and 55°C were determined under the optimized experimental conditions. In order to determine the thermodynamic constants (enthalpy ( $\Delta H^\circ$ ), free energy ( $\Delta G^\circ$ ) and entropy ( $\Delta S^\circ$ ) changes), thermodynamics of adsorption were studied by applying Eq. 4 and 5<sup>56</sup>.

$$\Delta G^\circ = \Delta H - T\Delta S \quad (4)$$

$$\ln K_L = \frac{-(\Delta H^\circ)}{(R \times T)} + \frac{\Delta S^\circ}{R} \quad (5)$$

The mathematical formulas of thermodynamics are shown in Table 1.

Physical and chemical adsorptions are distinguished from the level of  $\Delta G^\circ$ . The value of  $\Delta G^\circ \geq -15$  kJ/mol defines the physical adsorption while the  $\Delta G^\circ \leq -30$  kJ/mol

**Table 2.** Modeling of Cu (II) and Ni(II) sorption isotherms according to the initial adsorbent concentrations

Freundlich		Langmuir		Temkin		D-R	
Cu(II)	Ni(II)	Cu(II)	Ni(II)	Cu(II)	Ni(II)	Cu(II)	Ni(II)
$R^2=0.978$ $n=2.155$ $K_F=8.48$	$R^2=0.968$ $n=0.6968$ $K_F=0.312$	$R^2=0.978$ $K_L=5.849$ $q_{\max}=6.978$ $R_L=6.84 \times 10^{-3}$	$R^2=0.744$ $K_L=-43.36$ $q_{\max}=0.657$ $R_L=9.23 \times 10^{-4}$	$R^2=0.972$ $A_T=1.580$ $B=9.148$ $b_T=279.9$	$R^2=0.8957$ $A_T=0.147$ $B_T=20.708$ $b_T=123.66$	$R^2=0.859$ $q_0=25.71$ $\beta=-0.9268$ $E=0.7345$	$R^2=0.9106$ $q_0=28.036$ $\beta=-20.468$ $E=0.1562$

**Table 3.** Modeling of Cu(II) and Ni(II) sorption isotherms according to the initial adsorbate concentrations

Freundlich		Langmuir		Temkin		D-R	
Cu(II)	Ni(II)	Cu(II)	Ni(II)	Cu(II)	Ni(II)	Cu(II)	Ni(II)
$R^2=0.905$ $n=2.217$ $K_F=2.824$	$R^2=0.810$ $n=2.210$ $K_F=3.214$	$R^2=0.9908$ $K_a=3.523$ $q_{\max}=8.787$ $R_L=11.10^{-3}$	$R^2=0.8486$ $K_a=2.868$ $q_{\max}=4.717$ $R_L=13.7 \times 10^{-3}$	$R^2=0.986$ $A_T=3.513$ $B=6.2483$ $b=409.8$	$R^2=0.6767$ $A_T=1.699$ $B=3.5844$ $b=713.6$	$R^2=0.9371$ $q_0=22.49$ $\beta=3.5844$ $E=1.2565$	$R^2=0.6965$ $q_0=11.46$ $\beta=-0.6672$ $E=0.866$

**Table 4.** Kinetic constants for adsorption of Cu(II) onto the PWB

Cu(II) mg/L	$q_{\text{e,exp}}$ mg/g	Pseudo first-order			Pseudo second-order			Intra particle diffusion		Elovich		
		$k_1$	$q_e$	$R^2$	$k_2$	$q_e$	$R^2$	$k_{\text{id}}$	$R^2$	$\alpha$	$\beta$	$R^2$
25	17.60	0.1073	11.3	0.93	0.0199	18.518	0.99	1.2162	0.93	187.06	0.4816	0.95
35	18.85	0.0573	7.53	0.95	0.0222	19.305	0.99	1.2646	0.89	186.18	0.4495	0.96
45	20.10	0.0460	8.46	0.86	0.0136	21.052	0.99	1.6364	0.91	259.08	0.8021	0.95

**Table 5.** Kinetic constants for adsorption of Ni(II) onto the PWB

Ni mg/L	$q_{\text{e,exp}}$ mg/g	Pseudo first-order			Pseudo second-order			Intra particle diffusion		Elovich		
		$k_1$	$q_e$	$R^2$	$k_2$	$q_e$	$R^2$	$k_{\text{id}}$	$R^2$	$k_2$	$\beta$	$k_1$
25	11.6	0.0368	4.01	0.8699	0.0309	11.82	0.9989	0.5955	0.6459	43.65	0.6564	0.8926
35	12.3	0.0246	5.06	0.9131	0.0170	12.5	0.9974	0.6362	0.8858	59.96	0.6974	0.9501
45	12.9	0.0283	5.03	0.902	0.0179	13.10	0.997	0.5748	0.9233	222.17	0.7819	0.9653

**Table 6.** Thermodynamic parameter of Cu(II) and Ni(II) biosorption onto PWB

Metals	$\Delta H^\circ$ [kJ/mol]	$\Delta S^\circ$ [kJ/mol.K]	$\Delta G^\circ$ [kJ/K.mol]					
			293 K	298 K	303 K	308 K	313 K	318 K
Cu (II)	12.34	0.050	-2.31	-2.56	-2.81	-3.06	-3.31	-3.56
Ni (II)	12.42	0.039	1.025	0.83	0.636	0.442	0.247	0.05

shows chemical adsorption<sup>52</sup>. The values of  $\Delta G^\circ$  for Cu(II) was lower than zero while  $\Delta H$  and  $\Delta S^\circ$  were 12.34 kJ/mol and  $\Delta S^\circ = 0.05$  kJ/mol, respectively (Table 6). The negative value of  $\Delta G^\circ$  (ranges from  $-2.31$  to  $-4.06$  kJ/K · mol) is suggesting a physical adsorption process enhanced by electrostatic effect. The negative sign of  $\Delta G^\circ$  indicates spontaneous nature of the reaction while positive values of  $\Delta H$  confirm its endothermicity<sup>53</sup>.

The  $\Delta G^\circ$  value was higher than zero for the Ni(II) ions. When the  $\Delta G^\circ$  is higher than zero, it is indicated that the adsorption is not spontaneous thermodynamically<sup>3</sup>.  $\Delta S$  is also positive indicates an overall entropy increases<sup>48, 52, 57, 58</sup>.

From the rate of constant of Freundlich isotherm model, the activation energy ( $E_a$ ) for the adsorption is determined by using Arrhenius Eq. (6)

$$\ln K_2 = \ln A - \frac{-(E_a)}{(R \times T)} \quad (6)$$

where A refer to the Arrhenius factor.

For the PWB,  $E_a$  value was about 12.4 kJ/mol for adsorption. The calculated  $E_a$  value signifies the role of diffusion-controlled and physical adsorption processes in the rate-limiting of Cu(II) and Ni(II) ions sorption onto the PWB<sup>59</sup>.

### Sorption and desorption cycle

Nickel has a relatively elevated price<sup>60</sup> and the rinse water of electroplating industry contains up to the concentrations of 1000 mg/L<sup>61</sup>. In order to reduce the nickel cost of electroplating industry, recovery of nickel from the rinse water baths is very important<sup>62, 63, 64</sup>. Considering the cost of nickel, recovery from the PWB was investigated in this study.

Once the adsorption experiments completed, the PWB was drawn from the unit for reuse in a sorption. For the aqueous of HCl and H<sub>2</sub>SO<sub>4</sub> desorption studies, the pH of solution was about 1.0. By using Eq 7 percent desorption recovery was calculated.

$$\text{Recovery (\%)} = \frac{\text{amount of Cu(II)/Ni(II) desorbed}}{\text{amount of Cu(II)/Ni(II) adsorbed}} \quad (7)$$

About 71% and 59% recovery of Ni(II) was observed by using HCl and H<sub>2</sub>SO<sub>4</sub> desorption agents, respectively. Desorption percent of Ni(II) from the PWB with distilled water was about 11% which was almost negligible which was consistent with literature<sup>36, 65, 66</sup>. Due to the high amount of protons in dissolution, the metal recovery from the activated sludge is increased with decreasing pH in the solution<sup>22</sup>.

Results indicated that an ion exchange process between protons of the solution at low pH and Ni(II) of the active groups of biomass which was consistent with literature<sup>22, 36</sup>. The sorption capacity of PWB was decreased from 13 mg/g to 3.4 mg/g and 11.55 mg/g to 8.2 mg/g for the HCl and H<sub>2</sub>SO<sub>4</sub> desorbing agent, respectively. The loss of biosorption capacity of PWB by HCl and H<sub>2</sub>SO<sub>4</sub> agents was about 74% and 29%, respectively. Desorption experimental results indicated that the reuse of PWB in a new sorption-desorption cycle is not feasible due to the low adsorption capacity. It was assumed that the PWB structure was damaged at low pH condition for that reason reuse of PWB under the studied condition was not possible considering

adsorption capacity of the PWB. The same observation was reported by Hammami *et al.*<sup>22</sup>.

### CONCLUSION

Experimental results indicated that the PWB is an attractive adsorbent for Cu(II) and Ni(II) removal from the industrial wastewater. The maximum adsorption capacity of 18.9 mg Cu(II)/g and 13.5 mg Ni(II)/g was obtained at the contact time of 60 min and 120 min, respectively. The highest Ni(II) and Cu(II) removal efficiency of 54% and 65.4% was determined at the initial solution pH of 7.0 and 3.0, respectively. For the experimental conditions, the rate of adsorption was found to follow the pseudo-second-order kinetic. The biosorption of Cu(II) and Ni(II) onto the PWB were the endothermic process. The positive value of  $\Delta S$  for Ni(II) and Cu(II) revealed the increased randomness at the solid/liquid interface during the biosorption process. The results confirmed that the PWB could be used as an effective, cheap and easily applicable adsorbent for Cu(II) and Ni(II) removal without any treatment. Although the Ni(II) ions can be effectively recovered from the PWB by using HCl and H<sub>2</sub>SO<sub>4</sub> as desorbing agent, the PWB cannot be reused for adsorption because of the structure deterioration.

### ACKNOWLEDGMENTS

This study was supported by The Research Fund of Cumhuriyet University (CUBAP) under Grant No. M-548, Sivas, Turkey.

### LITERATURE CITED

- Pagnanelli, F., Mainelli, S., Bornoroni, L., Dionisi, D. & Toro, L. (2009). Mechanisms of heavy-metal removal by activated sludge. *Chemosphere*. 75, 1028–1034. DOI: 10.1016/j.chemosphere.2009.01.043.
- Markou, G., Mitrogiannis, D., Çelekli, A., Bozkurt, H., Georgakakis, D. & Chrysikopoulos, C.V. (2015). Biosorption of Cu<sup>2+</sup> and Ni<sup>2+</sup> by *Arthrospira platensis* with different biochemical compositions. *Chem. Eng. J.* 259, 806–813. [https://DOI.org/10.1016/j.cej.2014.08.037](https://doi.org/10.1016/j.cej.2014.08.037)
- Azouaou, N., Sadaoui, Z., Djaafri, A. & Mokaddem, H. (2010). Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics. *J. Hazard. Mater.* 184(1), 126–134. [https://DOI.org/10.1016/j.jhazmat.2010.08.014](https://doi.org/10.1016/j.jhazmat.2010.08.014)
- Jai, P.H., Wook, J.S., Kyu, Y.J., Gil, K.B. & Mok, L.S. (2007). Removal of heavy metals using waste eggshell. *J. Environ. Sci.* 19(12), 1436–1441. [http://dx.Doi.org/10.1016/S1001-0742\(07\)60234-4](http://dx.doi.org/10.1016/S1001-0742(07)60234-4)
- Aslan, S., Ozturk, M. & Yildiz, S. (2016). Sorption of heavy metals on biosludge. *Eur. Sci. J.* ESJ, 12(10), ISSN: 1857–7881 (Print), ISSN: 1857–7431 (Online).
- Jianlong, W., Yi, Q., Horan, N. & Stentiford, E. (2000). Bioadsorption of pentachlorophenol (PCP) from aqueous solution by activated sludge biomass. *Bioresour. Technol.* 75(2), 157–161. [https://DOI.org/10.1016/S0960-8524\(00\)00041-9](https://doi.org/10.1016/S0960-8524(00)00041-9)
- Liu, D., Tao, Y., Li, K. & Yu, J. (2012). Influence of the presence of three typical surfactants on the adsorption of nickel (II) to aerobic activated sludge. *Bioresour. Technol.* 126, 56–63. [http://dx.Doi.org/10.1016/j.biortech.2012.09.025](http://dx.doi.org/10.1016/j.biortech.2012.09.025)
- Pamukoglu, M.Y. & Kargi, F. (2006). Removal of copper (II) ions from aqueous medium by biosorption onto powdered waste sludge. *Process Biochem.* 41(5), 1047–1054. [https://DOI.org/10.1016/j.procbio.2005.11.010](https://doi.org/10.1016/j.procbio.2005.11.010)

9. Wei, D., Zhang, K., Wang, S., Sun, B., Wu, N., Xu, W., Du, B. & Wei, Q. (2017). Characterization of dissolved organic matter released from activated sludge and aerobic granular sludge biosorption processes for heavy metal treatment via a fluorescence approach. *Int. Biodeterior. Biodegrad.* 124, 2017. 326–333. <https://DOI.org/10.1016/j.ibiod.2017.03.018>
10. Yuncu, B., Sanin, F.D. & Yetis, U. (2006). An investigation of heavy metal biosorption in relation to C/N ratio of activated sludge. *J. Hazard. Mater.* 137(2), 990–997. <https://DOI.org/10.1016/j.jhazmat.2006.03.020>
11. Zhou, Y., Zhang, Z., Zhang, J. & Xia, S. (2016). New insight into adsorption characteristics and mechanisms of the biosorbent from waste activated sludge for heavy metals. *J. Environ. Sci.*, 45, 248–256. <https://DOI.org/10.1016/j.jes.2016.03.007>
12. Filipkowska, U. & Kuczajowska-Zadrożna, M. (2016). Investigation of the adsorption/desorption equilibria of Cd (II), Zn (II) and Cu (II) ions on/from immobilized digested sludge using biosurfactants. *Environ. Earth Sci.* 75(9), 814. DOI: 10.1007/s12665-016-5674-6.
13. Weng, C.H., Chang, E.E. & Chiang, P.C. (2001). Characteristics of new coccine dye adsorption onto digested sludge particulates. *Water Sci. Technol.* 44(10), 279–284.
14. Cojocaru, C., Diaconu, M., Cretescu, I., Savić, J. & Vasić, V. (2009). Biosorption of copper (II) ions from aqua solutions using dried yeast biomass. *Colloids Surf. A: Physicochemical and Engineering Aspects*, 335(1), 181–188. <https://DOI.org/10.1016/j.colsurfa.2008.11.003>
15. Kumar, R. Bishnoi, N.R. & Bishnoi, K. (2008). Biosorption of chromium (VI) from aqueous solution and electroplating wastewater using fungal biomass. *Chem. Eng. J.* 135(3), 202–208. <https://DOI.org/10.1016/j.cej.2007.03.004>
16. Tunali, Y., Karaca, H., Tay, T., Kivanç, M. & Bayramoglu, G. (2009). Biosorption of Pb (II) from aqueous solutions by a fungal biomass in a batch system: Equilibrium and kinetic studies, *Asian J. Chem.* 21(8), 6015.
17. Zhang, Q., Hu, J., Lee, D.J., Chang, Y. & Lee, Y.J. (2017). Sludge treatment: Current research trends, *Bioresour. Technol.* 243, 1159–1172, <http://dx.DOI.org/10.1016/j.biortech.2017.07.070>
18. Alexandre, V.M.F., Castro, T.M.S., Araújo, L.V., Santiago, V.M.J., Freire, D.M.G. & Cammarota, M.C. (2015). Minimizing solid wastes in an activated sludge system treating oil refinery wastewater. *Chem. Eng. Process.* <http://dx.DOI.org/10.1016/j.cep.2015.10.021>.
19. Li, C. & Ju, L.K. (2018). Enhancement of resource recovery and sludge digestion by cultivation of phagotrophic algae with alkali-pretreated waste activated sludge and waste ketchup. *Process Saf. Environ. Prot.* 113 233–241. <https://DOI.org/10.1016/j.psep.2017.10.004>
20. Abdelfattah, I., Ismail, A.A., Sayed, F.A., Almedolab, A. & Aboelghait, K.M. (2016). Biosorption of heavy metals ions in real industrial wastewater using peanut husk as efficient and cost effective adsorbent. *Environ. Nanotechnol. Monit. Man.* 6: 176–183. <http://dx.DOI.org/10.1016/j.enmm.2016.10.007>
21. Nuhoglu, Y. & Oguz, E. (2003). Removal of copper(II) from aqueous solutions by biosorption on the cone biomass of Thuja orientalis. *Process Biochem.* 38, 1627–1631. DOI: 10.1016/S0032-9592(03)00055-4.
22. Hammami, A., Gonzalez, F., Ballester, A., Blazquez, M.L. & Munoz, J.A. (2007). Biosorption of heavy metals by activated sludge and their desorption characteristics. *J. Environ. Manage.* 84, 419–426. DOI: 10.1016/j.jenvman.2006.06.015.
23. Kargi, F. & Cikla, S. (2006). Biosorption of zinc(II) ions onto powdered waste sludge (PWS): Kinetics and isotherms. *Enzyme Microb. Technol.* 38, 705–710. DOI: 10.1016/j.enzmictec.2005.11.005
24. Laurent, J., Casellas, M., Pons, M.N. & Dagot, C. (2010). Cadmium biosorption by ozonized activated sludge: The role of bacterial flocs surface properties and mixed liquor composition. *J. Hazard. Mater.* 183, 256–263. DOI: 10.1016/j.jhazmat.2010.07.019.
25. Ong, S.A., Toorisaka, E., Hirata, M. & Hano, T. (2013). Comparative study on kinetic adsorption of Cu(II), Cd(II) and Ni(II) ions from aqueous solutions using activated sludge and dried sludge. *App. Water Sci.* 3, 321–325. DOI: 10.1007/s13201-013-0084-3.
26. Rao, P.R. & Bhargavi, C. (2013). Studies on biosorption of heavy metals using pretreated biomass of fungal species. *Int. J. Chem. Chem. Eng.* 3(3), 171–180, ISSN 2248-9924.
27. Yang, C., Wang, J., Lei, M., Xie, G., Zeng, G. & Luo, S. (2010). Biosorption of zinc (II) from aqueous solution by dried activated sludge. *J. Environ. Sci.* 22(5), 675–680. [https://DOI.org/10.1016/S1001-0742\(09\)60162-5](https://DOI.org/10.1016/S1001-0742(09)60162-5)
28. Goodwin, J.A.S. & Forster, C.F. (1985). A further examination into the composition of activated sludge surfaces in relation to their settlement characteristics. *Water Res.* 19(4), 527–533. [https://DOI.org/10.1016/0043-1354\(85\)90045-4](https://DOI.org/10.1016/0043-1354(85)90045-4)
29. Horan, N.J. & Eccles, C.R. (1986). Purification and characterization of extracellular polysaccharide from activated sludges. *Water Res.* 20(11), 1427–1432. [https://DOI.org/10.1016/0043-1354\(86\)90142-9](https://DOI.org/10.1016/0043-1354(86)90142-9)
30. Chang, D., Fukushi, K. & Ghosh, S. (1995). Stimulation of activated sludge cultures for enhanced heavy metal removal. *Water Environ. Res.* 67(5), 822–827. <https://DOI.org/10.2175/106143095X131745>
31. Durmaz, B. & Sanin, F.D. 2001. Effect of carbon to nitrogen ratio on the composition of microbial extracellular polymers in activated sludge. *Water Sci. Technol.* 44(10), 221–229.
32. APHA, AWWA, WPCF (1995) Standard Methods for the Examination of water and wastewater, 19th ed. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, USA.
33. Jamshidi, M., Jamshidi, A. & Mehrdadi, N. (2012). Application of sewage dry sludge in concrete mixtures. *Asian J. Civil Eng (building and housing)*, 13(3), 365–375.
34. Mojapelo, S.K. (2017). Characterisation of wastewater dry sludge for lightweight concrete application, Faculty of Engineering and The Built Environment, Tshwane University of Technology, Master Thesis, 107 p.
35. Mun, K.J. (2007). Development and tests of lightweight aggregate using sewage sludge for nonstructural concrete. *Construct. Built. Mater.* 21(7), 1583–1588. <https://DOI.org/10.1016/j.conbuildmat.2005.09.009>
36. Ata, A., Nalcaci, O.O. & Ovez, B. (2012). Macro algae *Gracilaria verrucosa* as a biosorbent: A study of sorption mechanisms. *Algal Res.* 1(2), 194–204. <https://DOI.org/10.1016/j.algal.2012.07.001>.
37. Chen, H., Dou, J. & Xu, H. (2017). Removal of Cr (VI) ions by sewage sludge compost biomass from aqueous solutions: Reduction to Cr (III) and biosorption. *Appl. Surf. Sci.* 425, 728–735. <http://dx.DOI.org/10.1016/j.apsusc.2017.07.053>
38. Rocha, C.G., Zaia, D.A.M., da Silva Alfaya, R.V. & da Silva Alfaya, A.A. (2009). Use of rice straw as biosorbent for removal of Cu (II), Zn (II), Cd (II) and Hg (II) ions in industrial effluents. *J. Hazard. Mater.* 166(1), 383–388. <https://DOI.org/10.1016/j.jhazmat.2008.11.074>
39. Nouha, K., Hoang, N.V. & Tyagi, R.D. (2016). Fourier transform infrared spectroscopy and liquid chromatography–mass spectrometry study of extracellular polymer substances produced on secondary sludge fortified with crude glycerol. *J. Mater. Sci. Eng.* 5:3. <http://dx.DOI.org/10.4172/2169-0022.1000240>
40. Yahaya, Y.A., Don, M.M. & Bhatia, S. (2009). Biosorption of copper (II) onto immobilized cells of *Pycnoporus sanguineus* from aqueous solution: Equilibrium and kinetic studies. *J. Hazard. Mater.* 161(1), 189–195. <https://DOI.org/10.1016/j.jhazmat.2008.03.104>
41. Badireddy, A.R., Chellam, S., Gassman, P.L., Engelhard, M.H., Lea, A.S. & Rosso, K.M. (2010). Role of extracellular polymeric substances in bioflocculation of activated sludge microorganisms under glucose-controlled conditions. *Wa-*

- ter Res. 44(15), 4505–4516. <https://DOI.org/10.1016/j.watres.2010.06.024>
42. Yin, C., Meng, F. & Chen, G.H. (2015). Spectroscopic characterization of extracellular polymeric substances from a mixed culture dominated by ammonia-oxidizing bacteria. *Water Res.* 68, 740–749. <http://dx.DOI.org/10.1016/j.watres.2014.10.046>
43. Chassary, P., Vincent, T. & Guibal, E. (2004). Metal anion sorption on chitosan and derivative materials: a strategy for polymer modification and optimum use. *React. Funct. Polym.* 60, 137–149. <https://DOI.org/10.1016/j.reactfunctpolym.2004.02.018>
44. Guzman, J., Saucedo, I., Revilla, J., Navarro, R. & Guibal, E. (2003). Copper sorption by chitosan in the presence of citrate ions: influence of metal speciation on sorption mechanism and uptake capacities. *Int. J. Biol. Macromolecules.* 33(1), 57–65. [https://DOI.org/10.1016/S0141-8130\(03\)00067-9](https://DOI.org/10.1016/S0141-8130(03)00067-9)
45. Bermúdez, Y.G., Rico, I.L.R., Bermúdez, O.G. & Guibal, E. (2011). Nickel biosorption using *Gracilaria caudata* and *Sargassum muticum*. *Chem. Eng. J.* 66, 122–131. <http://dx.DOI.org/10.1016/j.cej.2010.10.038>
46. Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J. & Tchobanoglous, G. (2005). *Water Treatment: Principles and Design*, 2<sup>nd</sup> Edition, John Wiley and Son, Inc. 1947p.
47. Aslan, S. & Topcu, U.S. (2015). Adsorption of nickel and copper from water by waste nitrification organisms, ISITES2015-3<sup>rd</sup> International Symposium on Innovative Technologies in Engineering and Science, pp: 1955–1963, Valencia, Spain, 2015.
48. Katal, R., Baei, M.S., Rahmati, H.T. & Esfendian, H. (2012). Kinetic, isotherm, and thermodynamic study of nitrate adsorption from aqueous solution using modified rice husk. *J. Industrial Chem.* 18, 295–302. <http://dx.DOI.org/10.1016/j.jiec.2011.11.035>
49. Demirbas, E., Dizge, N., Sulak, M.T. & Kobya, M. (2009). Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. *Chem. Eng. J.* 148(2), 480–487. <https://DOI.org/10.1016/j.cej.2008.09.027>
50. Aslan, S., Polat, A. & Topcu, U.S. (2015), Assessment of the adsorption kinetics, equilibrium and thermodynamics for the potential removal of Ni<sup>2+</sup> from aqueous solution using waste eggshell. *Journal of Environmental Engineering and Landscape Management*, 23:3, 221–229, DOI: 10.3846/16486897.2015.1005015.
50. Kilic, M., Varol, E.A. & Putun, A.E. (2011). Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: equilibrium, kinetics and thermodynamics. *J. Hazard. Mater.* 189, 397–403. <http://dx.DOI.org/10.1016/j.jhazmat.2011.02.051>
52. Sljivic, M., Smiciklas, I., Plecas, I. & Mitric, M. (2009). The influence of equilibration conditions and hydroxyapatite physico-chemical properties onto retention of Cu<sup>2+</sup> ion. *Chem. Eng. J.* 148, 80–88. <http://dx.DOI.org/10.1016/j.cej.2008.08.003>
53. Ghasemi, Z., Seif, A., Ahmadi, T.S., Zargar, B., Rashidi, F. & Rouzbahani, G.M. (2012). Thermodynamic and kinetic studies for the adsorption of Hg (II) by nano-TiO<sub>2</sub> from aqueous solution. *Adv. Powder Technol.* 23(2), 148–156. <https://DOI.org/10.1016/j.apt.2011.01.004>
54. Rahchamani, J., Mousavi, H.Z. & Behzad, M. (2011). Adsorption of methyl violet from aqueous solution by polyacrylamide as an adsorbent: Isotherm and kinetic studies. *Desalination*, 267(2), 256–260. <https://DOI.org/10.1016/j.desal.2010.09.036>
55. Doğan, M., Ozdemir, Y. & Alkan, M. (2007). Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. *Dyes Pig.* 75(3), 701–713. <https://DOI.org/10.1016/j.dyepig.2006.07.023>
56. Mezenner, N.Y. & Bensmaili, A. (2009). Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste. *Chem. Eng. J.* 147(2), 87–96. <https://DOI.org/10.1016/j.cej.2008.06.024>
57. Ahmad, R., Kumar, R. & Haseeb, S. (2012). Adsorption of Cu<sup>2+</sup> from aqueous solution onto iron oxide coated eggshell powder: Evaluation of equilibrium, isotherms, kinetics, and regeneration capacity. *Arabian J. Chem.* 5, 353–359. <https://DOI.org/10.1016/j.arabjc.2010.09.003>
58. Chairat, M., Rattanaphani, S., Bremner, J.B. & Rattanaphani, V. (2005). An adsorption and kinetic study of lac dyeing on silk. *Dyes Pig.* 64, 231–241. <http://dx.DOI.org/10.1016/j.dyepig.2004.06.09>
59. Ayoob, S., Gupta, A.K., Bhakat, P.B. & Bhat, V.T. (2008). Investigations on the kinetics and mechanisms of sorptive removal of fluoride from water using alumina cement granules. *Chem. Eng. J.* 140(1), 6–14. <https://DOI.org/10.1016/j.cej.2007.08.029>
60. Coman, V., Robotin, B. & Ilea, P. (2013). Nickel recovery/removal from industrial wastes: A review. *Resour. Conserve. Recycle.* 73, 229–238. <https://DOI.org/10.1016/j.resconrec.2013.01.019>
61. Wardani, A.K., Hakim, A.N., Khoiruddin, Destifen, W., Goenawan, A. & Wenten, I.G. (2017). Study on the influence of applied voltage and feed concentration on the performance of electrodeionization in nickel recovery from electroplating wastewater, Proceedings of the 1<sup>st</sup> International Process Metallurgy Conference (IPMC 2016) AIP Conf. Proc. 1805. DOI: 10.1063/1.4974415.
62. Davidson, J. (2010). Removal of nickel (II) from aqueous solutions by polymer-enhanced ultrafiltration, A major qualifying project submitted to the faculty of Worcester Polytechnic Institute in partial fulfillment of the requirements for the Bachelor of Science Degree, Shanghai, China Project Center 73 p.
63. Dhokpande, S. & Kaware, J. (2016). Regeneration and recovery of nickel-a review. *Int. J. Sci. Eng. App. Sci.* (IJSEAS) – 2, 7, ISSN: 2395-3470.
64. Ramamurthi, V., Priya, P.G., Saranya, S. & Basha, C.A. (2009). Recovery of nickel (II) ions from electroplating rinse water using hectorite clay. *Modern App. Sci.* 3(9), 37. <http://dx.DOI.org/10.5539/mas.v3n9p37>
65. Deng, L., Su, Y., Su, H., Wang, X. & Zhu, X. (2007). Sorption and desorption of lead (II) from wastewater by green algae *Cladophora fascicularis*. *J. Hazard. Mater.* 143 2007. 220–225. <https://DOI.org/10.1016/j.jhazmat.2006.09.009>
66. Gupta, V.K. & Rastogi, A. (2008). Sorption and desorption studies of chromium (VI) from nonviable cyanobacterium *Nostoc muscorum* biomass. *J. Hazard. Mater.* 154(1), 347–354. <https://DOI.org/10.1016/j.jhazmat.2007.10.032>