

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

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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 m²/g, 0.0053 cm³/g, and 41.4 nm, respectively. Considering the R² value, q_{exp} and q_{cal}, 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 1970s¹. 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 wastewater². 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^{3, 4}.

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^{1, 5–11}, digested sludge^{12, 13}, algae¹⁴, fungi^{15, 16}, 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 (CO₂, N₂ 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 world¹⁷. 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^{18, 19}. The dried dead waste biosludge has a large specific surface area which is used for the adsorption of pollutants from waters²⁰.

Because the waste dried sludge has been considered as a competitive, effective, and cheap adsorbent²¹, it has been widely used for adsorption of heavy metals for water treatments in recent years^{1, 8, 21–27}.

Most of the bacteria have cell wall which consists of carboxyl, acidic polysaccharides, amino acids and other components⁸. 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^{8, 10, 28, 29}.

Acclimation and stimulation of biomass by special nutrients enhance the biosorption of heavy metals in the aqueous solution³⁰. 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^{10, 30, 31}.

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 (ΔH°), free energy (ΔG°) and entropy (ΔS°) 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°C for 48 hours. Dried biomass was grounded into small pieces in a mortar to powder and sieved to constant sizes (250 μm) 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 H_2SO_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°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°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 H_2SO_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) analysis³² 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 SiO_2 crystals (quartz) which was consistent with the literature^{33–35}. Other

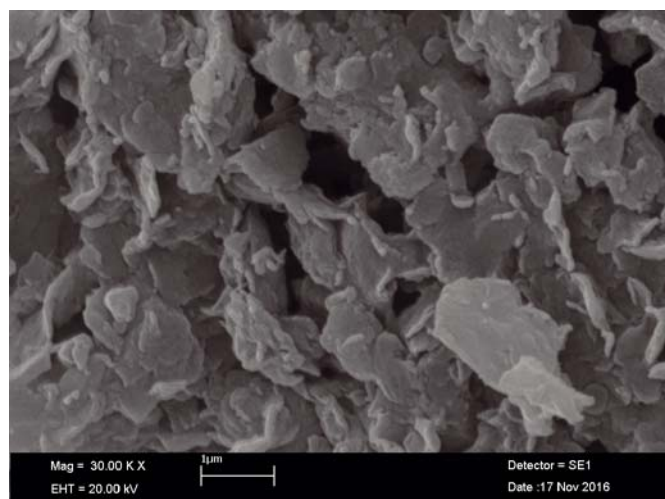


Figure 1. SEM images of raw PWB

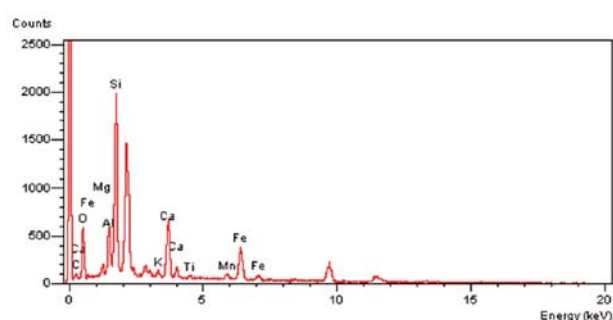
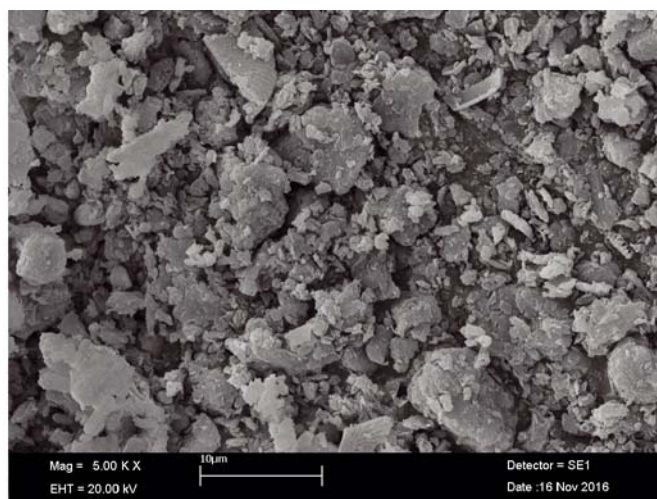


Figure 2. The EDX patterns of raw PWB

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 cm^{-1} could be attributed to the C-H and N-H stretching vibration. The bands at 2956 , 2918 , and 2849 cm^{-1} were assigned to the C-H stretching mode indicating material of the aliphatic nature^{1, 36-38}. The data at about 1633 cm^{-1} and 1538 cm^{-1} indicated to asymmetric and symmetric stretching of carboxylate, respectively¹. The peak at 1410 cm^{-1} could be attributed to the symmetric stretching of COO-group³⁹. The peak at 1037 cm^{-1} along with the peak at 1241 cm^{-1} could be attributed to C-O and C-N stretching vibration¹ and protein fractions⁴⁰. The fingerprint region between 900 and 600 cm^{-1} exhibited ring vibrations from aromatic amino acids and nucleotids⁴¹. The peaks between 897 cm^{-1} and 999 cm^{-1} were attributed to the O-P-O stretching in nucleic acids by Yin *et al.*⁴². Because of the dominant peak for SiO_2

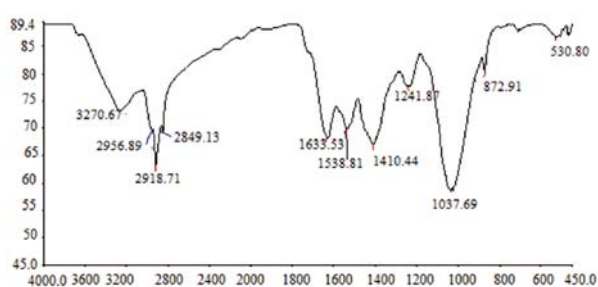


Figure 3. The FT-IR spectra of the PWB

was observed with the EDX analysis, the absorption bands at about 872 cm^{-1} and 530 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 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 adsorbent³. 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

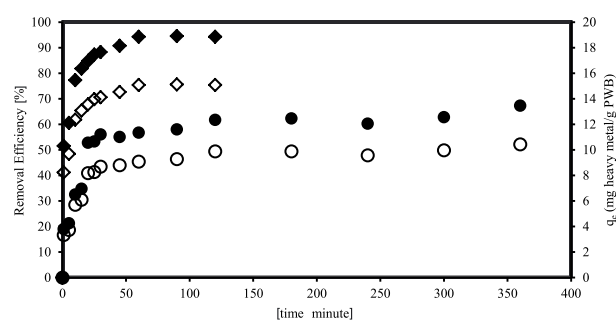


Figure 4. The effect of contact time on Cu(II) and Ni(II) removal by the PWB

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 dependent³⁸. Since pH effect the surface charge of sorbent, the adsorbate ionization state, and form of adsorbate^{8, 43, 44}, the pH of solution is one of the most important factors on the rate and the extent of adsorption⁸.

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.*⁴⁵ 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.

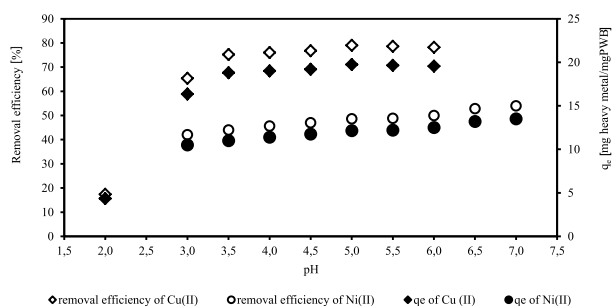


Figure 5. The effect of initial pH

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)₂ takes places at pH higher than 5.0 and precipitate at the pH value greater than 6.0⁴⁶ 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 NH₄-N concentrations at various pH were determined in the decant of batch units. Average concentrations of COD and NH₄-N were about 173 mg/L

and 2.9 mg/L, respectively. Release of organic matter and NH₄-N from the nitrification organism into the solution was also mentioned by Aslan and Topcu⁴⁷.

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 concentrations³, 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.

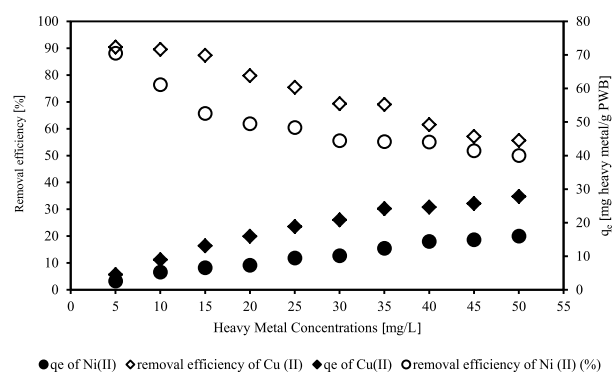


Figure 6. The effect of initial adsorbate concentrations

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.*⁴⁸ 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^{3, 8}.

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 temperature⁴⁹. However, the previous adsorption study indicated that the sorption capacity of biomass slightly

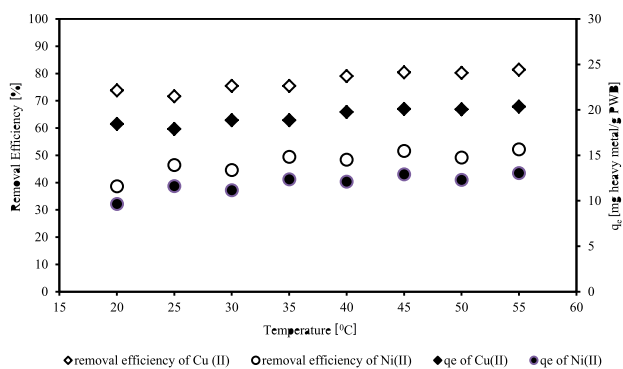


Figure 7. Temperature effect on the adsorption capacity of PWB

decreased when the temperature was higher than 60°C which might be denaturing of biomass wall structure¹¹.

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 $C_5H_7O_2N$ contains different organic and inorganic compounds. When the biomass is exposed to the extreme conditions, some of compounds (organic matter, NH_4-N , Ca^{2+} and Mg^{2+}) are released from the cell into the water^{5, 9, 24, 47}. It was found that the concentrations of COD and NH_4-N of water after adsorption increased with increasing temperature (Fig. 8). Elevating the temperature from 20 to 55°C, the release of COD (from

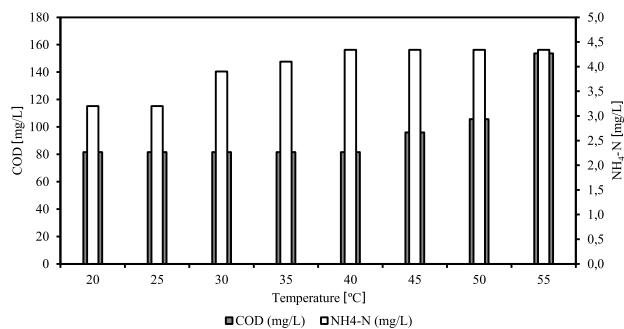


Figure 8. Temperature effect on the release of organic matter and NH_4-N

81.6 mg/L to 153.6 mg/L) and NH_4-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 kinetics⁵⁰

	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 ϵ^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^{50,51}.

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 unfavorable⁵². According to the Freundlich approach, uptake of adsorbate onto the adsorbent is increasing by increasing adsorbate concentrations in the solution⁵³.

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 rate⁵⁴. 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_{exp}) and calculated (q_{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 ions⁴⁵.

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 (ΔH°), free energy (ΔG°) and entropy (ΔS°) changes), thermodynamics of adsorption were studied by applying Eq. 4 and 5⁵⁶.

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

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

The mathematical formulas of thermodynamics are shown in Table 1.

Physical and chemical adsorptions are distinguished from the level of ΔG° . 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_{id}	R^2	α	β	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_{id}	R^2	k_2	β	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	ΔH° [kJ/mol]	ΔS° [kJ/mol.K]	ΔG° [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 adsorption⁵². The values of ΔG° for Cu(II) was lower than zero while ΔH and ΔS° were 12.34 kJ/mol and $\Delta S^\circ = 0.05$ kJ/mol, respectively (Table 6). The negative value of ΔG° (ranges from -2.31 to -4.06 kJ/K · mol) is suggesting a physical adsorption process enhanced by electrostatic effect. The negative sign of ΔG° indicates spontaneous nature of the reaction while positive values of ΔH confirm its endothermicity⁵³.

The ΔG° value was higher than zero for the Ni(II) ions. When the ΔG° is higher than zero, it is indicated that the adsorption is not spontaneous thermodynamically³. ΔS is also positive indicates an overall entropy increases^{48, 52, 57, 58}.

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 PWB⁵⁹.

Sorption and desorption cycle

Nickel has a relatively elevated price⁶⁰ and the rinse water of electroplating industry contains up to the concentrations of 1000 mg/L⁶¹. In order to reduce the nickel cost of electroplating industry, recovery of nickel from the rinse water baths is very important^{62, 63, 64}. 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 H₂SO₄ 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 H₂SO₄ 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^{36, 65, 66}. Due to the high amount of protons in dissolution, the metal recovery from the activated sludge is increased with decreasing pH in the solution²².

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^{22, 36}. 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 H₂SO₄ desorbing agent, respectively. The loss of biosorption capacity of PWB by HCl and H₂SO₄ 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.*²².

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 ΔS 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 H₂SO₄ as desorbing agent, the PWB cannot be reused for adsorption because of the structure deterioration.

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