Adsorption of Nickel and Copper from Water by Waste Nitrification Organisms

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Abstract:

The heavy metals; nickel and copper biosorption performance of waste nitrifying sludge was determined at various temperatures and pHs. It was found that the organic content and NH_4-N concentrations in the water increases with increasing the temperature. The sorption of heavy metals also increased with increasing the temperatures. The rise of adsorption with temperature may enlarge the pore size to some extent which may also affect the adsorption capacity of biosludges. The highest sorption capacity of bioslude was determined at the pH of 5.0. The data obtained from the experiments showed that the contact time of about 360 min and 1440 min were sufficient to achieve equilibrium time for nickel and copper, respectively.

Key words: Biosorption, copper, nickel, waste sludge

1. Introduction

Heavy metal contamination of the environment is a severe public health problem. An important source of water pollutants is industrial discharge wastewater which contains heavy metals. Most industrial wastewaters are discharged into the water body without proper management process. High concentrations of heavy metal affect negatively human, animal and vegetation in the water body. Because of unique characteristics of heavy metals, which are non-biodegradable and accumulated by living organisms, are the main environmental concerns [1].

Treatment of the wastewater including heavy metal ions became particularly difficult due to implementation of more restrict law regulations that control the concentration of pollutants in effluents discharged into waters and soil on the level lower than 1 mg/kg [2]. The treatment processes - such as such as ion exchange, chemical precipitation and coagulation- flocculation, membranes processes - for the removal of low concentrations of metal ions are often considered as an ineffective and/or very expensive method to achieve target level. Technical limitations, economical constraints, and environmental criteria are some issues that explain the need for alternative treatment processes for the removal of heavy metal in wastewater [3].

In last two decades, biosorption has been widely investigated for the removal of heavy metal. Microorganisms are found to be capable of efficiently accumulating heavy-metal ions. Among the numerous natural materials for removing heavy metals, biosorbents such as bacteria, fungi,

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and algae [4-7], yeast [8-10], waste tea [11, 12], bael tree leaf powder [13], sugarcane bagasse pith [14], *chlorella vulgaris* [8], eggshell [1,15] have attracted attention as a low-cost sorbents from wastewater. Adsorption potential of the waste biosolids is summarized in Table 1.

Table 1. Comparison of maximum monolayer adsorption on Ni (II) and Cu (II) ions onto various adsorbents

Biosorbents	**q_m (mgNi^{2+}/g)**	**q_m (mgCu^{2+}/g)**	**References**
Clarified sludge	14.3		[16]
Spirulina platensis	69.04		[17]
Acid-treated alga	44.247		[18]
Untreated alga	40.983		[18]
Green alga *Spirogyra*		133.3	[4]
Dried activated sludge		62.50	[19]
P. chrysosporium		248.15	[20]
Bacillus subtilis		146.09	[21]
Powdered waste activated sludge		117	[22]
Activated sludge		7.94	[23]
Ochrobactrum anthropi		32.6	[24]

In recent years, water pollutants removal by biosorption using waste sludge which is produced in the biological treatment plants is widely used in the laboratory studies [26-32]. The use of dead cell, which is waste materials, as metal binding compounds has been gaining advantage because it is not affected from the heavy metals. As a consequence, activated sludge produced in the biological treatment facilities of the treatment plant is considered as a good bioadsorbent for the removal of heavy metal ions from industrial wastewater [26].

Biological nitrification is a widely applied process in the wastewater treatment facilities. Aerobic autotrophic bacteria are responsible for nitrification in the biological processes. In the nitrification process, NH_4^+-N is first oxidized into NO_2-N by *nitrosomonas sp.* (ammonium oxidizing bacteria, AOB) and then NO_2-N is rapidly oxidized to NO_3-N by *nitrobacter sp.* (nitrite oxidizing bacteria, NOB). The overall stoichiometric equation of nitrification process can be written as [33];

$$NH_4 + 1.815\ O_2 + 0.1304\ CO_2 \longrightarrow 0.0261 C_5H_7O_2N + 0.973\ NO^-_3 + 0.921\ H_2O + 1.973\ H^+$$

(Equation 1)

As can be seen from the equation, about 25% of the consumed NH^+_4 is converted to the biomass in the nitrification process and excess biomass is disposed from the wastewater treatment plants.

The purpose of this investigation was to study the biosorption of Cu^{2+} and Ni^{2+} from synthetic water using nitrifying sludge obtained from a laboratory scale reactor. In this study, effects of the temperature and pH on the COD release from the biomass was investigated.

2. Materials and Method

2.1. Enrichment of microorganisms

Nitrifying sludge was obtained from the laboratory scale bioreactor which was operated about 5 years. The inorganic medium contained (in mg/L): NH_4Cl (764.3), Na_2EDTA (4.83), $CuSO_4$ (0.0046), Thiamine (0.1), $ZnSO_4.7H_2O$ (0.023), $CoCl_2.6H_2O$ (0.0119), $Na_2MoO_4.2H_2O$ (0.066), $MgSO_4.7H_2O$ (36.97), $NaHCO_3$ (226), $CaCl_2.2H_2O$ (36.74), H_3BO_3 (1.0), $FeCl_3.6H_2O$ (0.316), K_2HPO_4 (1960), and KH_2PO_4 (1920).

2.2. Preparation of adsorbent

The biomass was washed several times with tap and pure water to remove impurities. Water was evaporated at 60ºC on a water bath for about 48 h and the biomass was oven dried at 60ºC for 24 h. The dried biomass was crushed and sieved into several fractions.

2.3. Sorption Studies

The synthetic solutions were prepared by diluting Ni^{2+} and Cu^{2+} standard stock solutions (250 mg/L) obtained by dissolving known masses of $NiCl_2.6H_2O$ and $CuCl_2$ in the distilled water. A known amount of biomass (0,025 g) was used throughout the experiments. Final volumes of the solution was 100 mL. Experimental studies were carried in 250 mL glass-stoppered Erlenmeyer flasks. Batch experimental studies were performed in an orbital incubator shaker (Gerhardt) at a constant speed of 150 rpm. All solutions were prepared from analytical reagent chemicals. Fresh dilutions of the synthetic wastewater were used in the experiments.

Effects of temperature and pH on the sorption of heavy metals were tested at various levels. Initial pHs of the solutions were adjusted using H_2SO_4 or NaOH solutions. The batch units were agitated in an orbital incubator shaker for a contact time varied in the range 0–2880 min at various temperatures.

2.4. Analytical methods

In order to get supernatant liquids, the samples were centrifuged at 4000 rpm for 10 min (NF800, NUVE). Concentrations of Ni^{2+} and Cu^{2+} in the solutions were determined with a Merck photometer (PHARO100). A spectraquant analytical kits (Merck, 14785 and 14767) were used to measure Cu^{2+} and Ni^{2+} concentrations in the initial and final solutions. COD concentrations of the influent and effluent samples were determined according to standard methods [34]. Concentrations of NH_4-N in the clear sample was determined with Merck photometer (PHARO 100) using analytical kits; NH_4-N (14752). The analysis of samples was carried out at the ambient temperature.

3. Results and Discussion

The data obtained from the experiments showed that the contact time of about 360 min and 1440 min were sufficient to achieve equilibrium time for nickel and copper, respectively.

3.1. Effect of temperature

It was found that the concentrations of COD and NH_4-N in the water and sorption capacities of biosolids increased with increasing temperature (Figure 1 and 2). Cu^{2+} and Ni^{2+} ions uptake capacity of biosolids increased with increasing temperature up to 40 ^{0}C. At a temperature of about 20 ^{0}C, the removal efficiency of Cu^{2+} and Ni^{2+} at equilibrium was 88 % and 24%, respectively. The highest removal efficiencies (95 % for Cu (II) and 33% for Ni (II)) was achieved at the temperature of 40 ^{0}C.

Elevating the temperature from 20 to 40 ^{0}C, the release of organic contents into the aqueous solution increased from 6 to 11 mg COD/L. The value of q_e elevated from 0.098 to 0.132 g Ni(II)/g biosolids and from 0.348 to 0.37 g Cu (II)/g biosolids by increasing temperature from 20 to 40 ^{0}C. Results might be attributed to the creation of some new active sites on the biosolids and increase in collision frequency between adsorbent and heavy metal ions at high temperatures. In addition to that, the rise of adsorption with temperature may enlarge the pore size to some extent which may also affect the adsorption capacity [35].

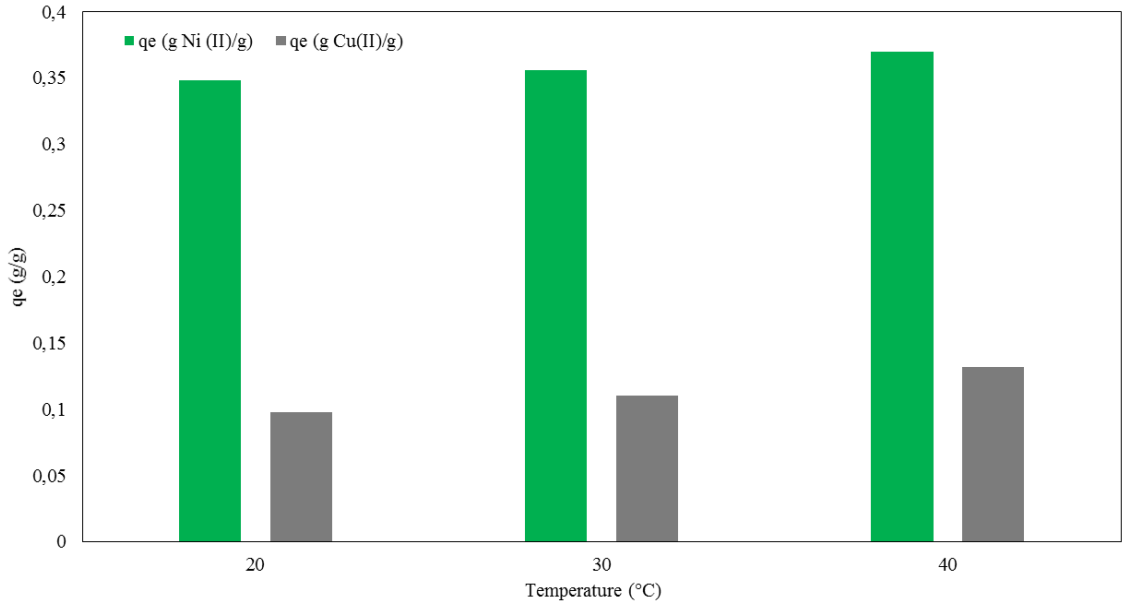

Figure 1. Effects of temperature on the sorption capacities

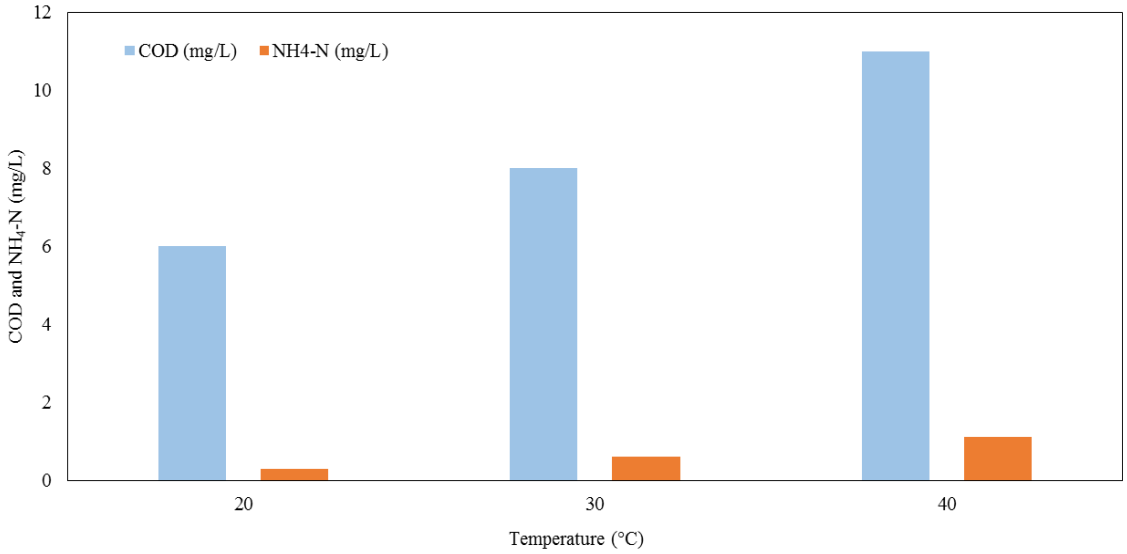

Figure 2. Temperature effects on the COD and NH_4-N concentrations

3.2. Heavy metal sorption at different initial pH

The acidity of solution is an important parameter for the sorption of heavy metals from aqueous solutions since the value of pH is responsible for protonation of metal binding sites, $Ni^{2+}$and Cu^{2+} speciation in the solution [2]. The uptake of heavy metals was investigated as the function of pH value of 3.0, 4.0 and 5.0.

Sorption of Ni^{2+} and Cu^{2+} after interaction of heavy metals and biosolids sorbent is presented in Figure 3. Heavy metal uptake by biosolids was a function of initial solution pH. The lowest

adsorption efficiency of 15% and 69% were observed at the pH value of 3.0 for Ni^{2+} and Cu^{2+}, respectively. Increasing the pH value of 5.0, sorption capacities (q_e) increased significantly to 0.122 g Ni(II)/g and 0.378 g Cu (II)/g. The ionization degree of heavy metal and the surface property of the biosolids may be affected by the pH. The concentration of COD and NH_4-N was significantly elevated at low pH (Figure 4).

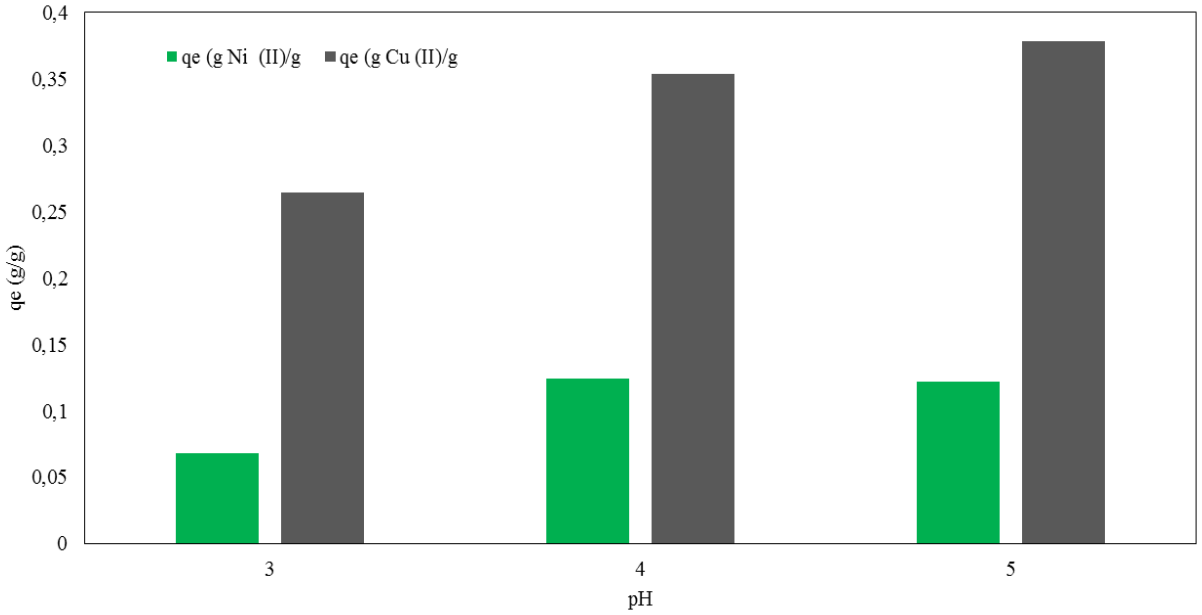

Figure 3. Effects of pH on the sorption capacities

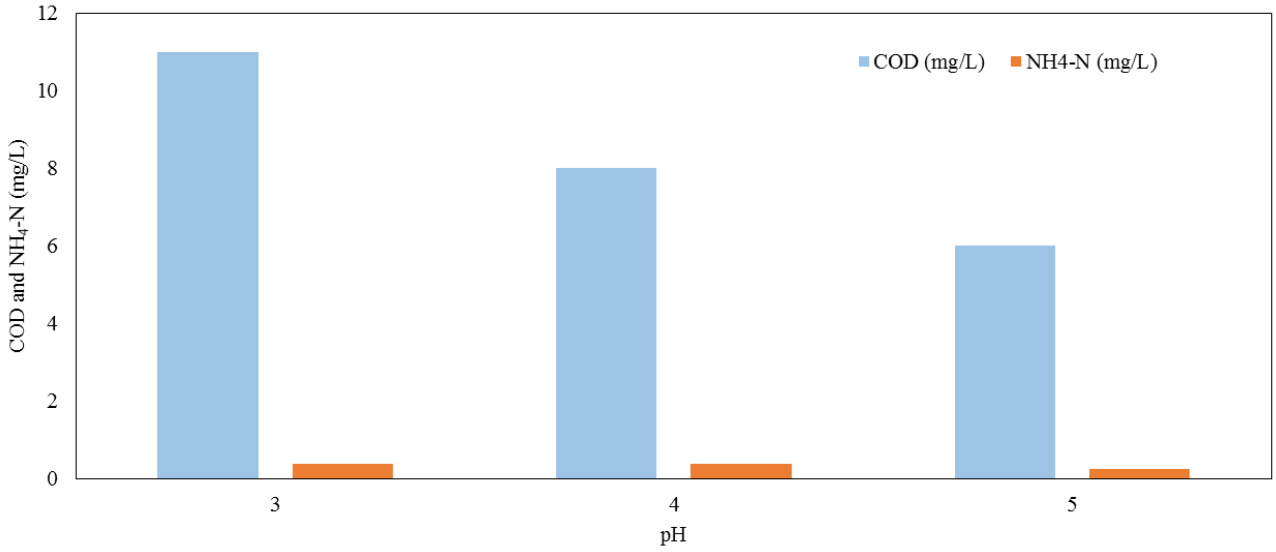

Figure 4. Effects of pH on the COD and NH_4-N concentrations

Conclusion

The possibility of use of waste dried nitrifying sludge to remove Cu (II) and Ni (II) ions from aqueous solution was investigated. Results indicating that the waste biosolids might be used for heavy metal removal from aqueous solution. The maximum sorption capacities were determined at the pH value of 5.0. Adsorption of Cu^{2+} and Ni^{2+} was highly temperature dependent. It was found that the organic content was increases with increasing the temperature. The sorption of heavy metals also increased with increasing the temperatures.

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