# **Adsorption Of Heavy Metals Onto Waste Tea**

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#### Abstract

Adsorption of Ni (II) and Cu (II) on the waste tea materials were studied at various temperatures and pHs. The maximum adsorption capacities of tea materials were as determined at the pH and temperature of 5.0 and 50  $^{\circ}$ C. Adsorption capacity of tea is more affected from pH than temperature. At the end of the batch experiments, concentration of NH<sub>4</sub>-N was lower than 1.0 mg/L. However, COD concentrations were increased from 88 mg/L to 96 mg/L by increasing temperatures from 30 to 50  $^{\circ}$ C, respectively. The highest organic matter release from the sorbent was observed at the pH of 2.0.

Keywords: Adsorption, Copper, Nickel, Heavy Metal, Waste tea

#### Introduction

Adsorption is the process of accumulating pollutants that are in solution on a suitable interface. In this process, a mass in the solution or air is transferred to the solid phase. Adsorption processes are used in drinking water treatment for the removal of taste–and odor causing compounds, synthetic organic chemicals, color–forming organics, and disinfection byproducts precursors (Crittenden et al., 2005). The adsorption process has not been used extensively in wastewater treatment. However, activated carbon treatment of wastewater is usually thought of a polishing process for water (Tchobanoglous et al., 2004).

The discharge of effluents containing heavy metals from a wide range of industries-electroplating, microelectronics, metal forming, paper, textiles, chemicals- is of concern to the public, industry and government alike (Cheung et al., 2000). Various wastewater treatment processes such as chemical precipitation, membrane separation, sorption/ion exchange, solvent extraction, phytoextraction, ultra filtration, reverse osmosis, and adsorption have been used to remove heavy metals from water and wastewater (Cheung et al., 2000; Kizilkaya et al., 2010). Chemical precipitation and electrochemical methods are become ineffective particularly when metal concentration in the water is too low. Additionally chemical precipitation produces large quantity of chemical sludge (Cojocaru et al., 2009). Some of the conventional methods such as ion exchange and activated carbon adsorption are extremely expensive processes when the wastewater containing trace concentration of heavy metals (Cojocaru et al., 2009; Jianlong et al., 2000; Demirbas, 2008; Kumar et al., 2011) Among the physico-chemical treatment processes, adsorption is found to be highly effective, cheap and easy to adapt (Seco et al., 1997). Although, the most widely studied adsorbent is an activated carbon (Corapcioglu and Huang, 1987; Seco et al., 1997), the application of waste materials for the removal of heavy metal from water has been much attention in last decades. When compared to activated carbon, the usage of waste materials as a low-cost adsorbent such as fish bones (Kizilkaya et al., 2009), untreated coffee grounds (Azouaou et al., 2010), organisms (Aslan and Topcu, 2015; Ozdemir et al., 2003; Pagnanelli et al., 2009), egg shell (Aslan et al., 2015; Polat and Aslan, 2014), black carrot residues (Guzel et al., 2008) has been received considerable attention to remove heavy metal ions from water and wastewaters by researchers.

In this experimental study, Cu(II) and Ni(II) adsorption capacity of the waste tea materials under various pHs and temperatures were investigated. Additionally, releases of organics and NH<sub>4</sub>-N from the waste tea under different conditions were determined.

# Materials and Methods Biosorbent Preparation

The waste tea materials was used for the adsorption of Cu(II) and Ni(II) from synthetic wastewater. After washing the waste tea with tap and pure waters, it was dried at about 105  $^{0}$ C in an oven. After adding tea in the water volume of 100 mL, the initial pH of water solution was adjusted to target values using H<sub>2</sub>SO<sub>4</sub> and NaOH solutions. The final pHs of the samples were determined after completing the batch experiments.

# **Adsorption Studies**

Ausorption Studies The stock solutions of Cu(II) and Ni(II), which were prepared using analytical grade of NiCl<sub>2</sub>.6H<sub>2</sub>O and CuCl<sub>2</sub> in demineralized water, was used throughout the experiments. The waste tea of 0.1 g was added into 100 mL demineralized water. Batch experiments were carried in 250 mL glassstoppered Erlenmeyer flasks. The adsorption uptake of the waste tea under the initial Cu(II) and Ni (II) concentration of 25 mg/L, agitation rate of 150 rpm was investigated. The maximum adsorption capacity was determined at the pH values varying between 2.0 and  $5.0\pm0.1$ , shaking the suspension for 2 hours at a temperature of  $40\pm1$  <sup>0</sup>C. The mixtures were stirred at the temperatures of 30, 40, and  $50\pm1$  <sup>0</sup>C at the pH value of 5.0. The aliquots of supernatant were withdrawn and centrifuged at 4000 rpm for 10 min (NF800, NUVE) for Ni(II) and Cu(II) analysis. Heavy metal concentrations were determined by using spectraquant analytical kits (Merck, 14785 and 14767) by a Merck photometer (PHARO100). The initial and final concentrations of COD were determined according to standard methods (APHA, 1995). The equilibrium adsorption capacity and removal efficiency of the waste tea were determined by the Equation I and II, respectively.

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

$$(E)(\%) = 100 \times (C_0 - C_e) / C_0$$
<sup>(2)</sup>

Where  $q_e$  is the sorption capacity, E is the removal efficiency,  $C_o$  and  $C_e$  are the initial and final concentrations of heavy metals in the solution, V(L) is the volume of solution and m (g) is the waste tea amount.

#### **Results and Discussion**

The equilibrium time was determined in 45 minutes for Cu(II) and Ni(II) at the agitation velocity of 150 rpm.

### Effects of pH

As pH in metal-containing wastewater can vary, experimental study at different pH values were tested to determine the effect of Cu(II) and Ni (II) sorption by waste tea materials. Water pH governs the speciation of metals and also the dissociation of active functional sites on the sorbent (Azouaou et al., 2010). The extractability of the heavy metals from water is pH dependent. In this study, initial pHs of water were adjusted to the value of 2.0, 3.0, and  $5.0\pm0.1$ . The effectiveness of the process is defined by the quantity adsorbed (mg/g) versus pH plot for Cu(II) and Ni(II) involved, as presented in Figure 1. The maximum adsorption capacity was determined at the pH value of 5.0 for Cu(II) and Ni (II). The sorption capacity of waste tea were 6.3 mg Cu(II)/ g sorbent and 8.8 mg Ni(II)/g sorbent at the pH 2.0. Increasing the initial pH of the solution from 2.0 to 5.0,  $q_e$  values reached to about 14.9 mg Cu(II)/g sorbent and 10.8 mg Ni(II)/g sorbent. At lower pH, the surface of the sorbents exhibits an increasing positive characteristic. H+ ions present at a higher concentration in the solution and compete with Cu(II) and Ni(II) ions for the active sites of sorbent resulting in the decreased uptake of heavy metal (Nuhoglu and Oguz, 2003). Significant pH variations

between initial and final solutions were not observed throughout the experimental studies.

At lower pH,  $H^+$  ions compete with metal cation for the exchange sites of the sorbents, thereby partially releasing the latter. The heavy metal cations are completely released under circumstances of extreme acidic conditions (Nuhoglu and Oguz, 2003).

Removal efficiencies of Cu(II) and Ni(II) were increased from about 25% to 60% and from 35% to 43% by increasing pH from 2.0 to 5.0, respectively. As can be seen in Figure 2, releases of organic matters and ammonium from the waste tea are increasing with decreasing pH.







Figure 2. Variations of COD and NH<sub>4</sub>-N concentrations under different pHs (Temperature =  $40^{\circ}$ C).

#### **Effects of Temperature**

The variations of  $q_e$  value at various temperatures under the adsorbent dosage of 1.0 g/L, initial Cu(II) and Ni(II) concentration of 25 mg/L, agitation speed of 150 rpm and initial pH of 5.0±0.1 are presented in Figure 3. Figure is revealing that the adsorption capacity of waste material at equilibrium slightly increased with increasing temperature from 30  $^{\circ}$ C to 50  $^{\circ}$ C. The values of  $q_e$  increased from 8.7 mg Ni(II)/g and 11.5 mg Cu(II)/g at 30  $^{\circ}$ C to 10.9 mg Ni(II)/g and 14.7 mg Cu(II)/g at 50  $^{\circ}$ C. After completing batch experiments, COD and NH<sub>4</sub>-N were detected in the waters. Although the concentrations of NH<sub>4</sub>-N was lower than 1.0 mg/L, COD concentrations increased from 88 mg/L to 96 mg/L by elevating the temperatures from 30 to 50  $^{\circ}$ C, respectively (Figure 4). Similar observation was observed by other studies and results attributed to the creation of some new active sites on the sorbents and increase in collision frequency between adsorbent and cations at high temperatures (Polat et al., 2014).

The highest removal efficiency of Cu(II) (59%) and Ni(II) (43%) were observed at the temperature of  $50^{\circ}$ C.





Figure 3. Effect of temperatures on the sorption capacity of waste tea.

Figure 4. Variations of COD and  $NH_4$ -N concentrations at various temperatures (initial pH= 5.0).

## Conclusion

The highest adsorption capacity for Cu (II) (14.9 mg/g) and Ni (II) (10.8 mg/g) at pH 5.0 were observed. Adsorption of Cu(II) and Ni(II) was not significantly affected from the temperature under experimental conditions. Significant concentration of organic matter was released from the waste materials. With a low-cost waste tea material, the adsorption process is a very useful method for removal of heavy metals from the wastewater.

# **References:**

APHA, AWWA, WPCF 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, 1995.

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(03): 221–229. http://dx.doi.org/10.3846/16486897.2015.1005015.

Azouaou, N., Sadaoui, Z., Djaafri, A.,& Mokaddem, H. (2010). Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics, *Journal of Hazardous Materials* 184, 126–134, doi:10.1016/j.jhazmat.2010.08.014.

Cojocaru, C., Diaconu, M., Cretescu, I., Savi, J., & Vasi, V. (2009). Biosorption of copper (II) ions from aqua solutions using dried yeast biomass. *Colloid Surface A*, 335, 181–188. doi:10.1016/j.colsurfa.2008.11.003

Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J.,& Tchobanoglous, G. (2005). Water Treatment: Pricciples and Design, 2<sup>nd</sup> Edition john Wiley& Son,Inc., 1947p.

Corapcioglu, M.O. & Huang, C.P. (1987). The adsorption of heavy metals onto hydrous activated carbon, *Water Research*, 21, 9, 1031–1044, doi:10.1016/0043-1354(87)90024-8

Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: A review, *Journal of Hazardous Materials*, 157, 220–229. doi:10.1016/j.jhazmat.2008.01.024

Guzel, F., Yakut, H., & Topal, G. (2008). Determination of kinetic and equilibrium parameters of the batch adsorption of Mn(II), Co(II), Ni(II) and Cu(II) from aqueous solution by black carrot (Daucus carota L) residues, *Journal of Hazardous Materials*, 153 (2008) 1275–1287. doi:10.1016/j.jhazmat.2007.09.087

Jianlong, W., Yi, Q., Horan, N., &Stentiford, E. (2000). Bioadsorption of Pentachlorophenol (PCP) from Aqueous Solution by Activated Sludge Biomass, *Bioresource Technology*, 75, 157-161. doi:10.1016/S0960-8524(00)00041-9.

Kizilkaya, B., Tekinay, A. A., & Dilgin, Y. (2010). Adsorption and Removal of Cu (II) ions from Aqueous Solution Using Pretreated Fish Bones. *Desalination* 264, 37–47. http://dx.doi.org/10.1016/j.desal.2010.06.076. Kumar, P. S., Ramalingam, S., Kirupha, S. D., Murugesan, A., Vidhyadevi,

Kumar, P. S., Ramalingam, S., Kirupha, S. D., Murugesan, A., Vidhyadevi, T.,& Sivanesan, S. (2011). Adsorption Behavior of Nickel(II) onto Cashew Nut Shell: Equilibrium, thermodynamics, kinetics, mechanism and process design, *Chemical Engineering Journal*, 167, 122–131. doi:10.1016/j.cej.2010.12.010.

Nuhoglu, Y., & Oguz, E. (2003). Removal of Copper(II) from Aqueous Solutions by Biosorption on the Cone Biomass of *Thuja Orientalis*, *Proses Biochemistry*, 38, 1627-1631. Doi:10.1016/S0032-9592(03)00055-4.

Ozdemir, G., Ozturk, T., Ceyhan, N., Isler, R., & Cosar, T.(2003). Heavy Metal Biosorption by Biomass of *Ochrobactrum Anthropi* Producing Exopolysaccharide in Activated Sludge, *Bioresource Technology*, 90, 71–74. doi:10.1016/S0960-8524(03)00088-9

Polat, A.,& Aslan, S. (2014). Kinetic and Isotherm Study of Cupper Adsorption from Aqueous Solution Using Waste Eggshell, *Journal of Environmental Engineering and Landscape Management* 22 (2):132–140. http://dx.doi.org/10.3846/16486897.2013.865631.

Rocha, C.G., Zaia, D.A.M., Alfaya, R.V.S., Alfaya, A.A.S. (2009). Use of Rice Straw as Biosorbent for Removal of Cu(II), Zn(II), Cd(II) and Hg(II) Ions in Industrial Effluents, *Journal of Hazardous Materials*, 166 (2009) 383–388, doi:10.1016/j.jhazmat.2008.11.074.

Seco, A., Marzal, P., Gabaldon, C., & Ferrer, J. (1997), Adsorption of Heavy Metals from Aqueous Solutions onto Activated Carbon in Single Cu and Ni Systems and in Binary Cu-Ni, Cu-Cd and Cu-Zn Systems, *Journal of Chemical Technology and Biotechnology*, 1997, 68, 23-30, DOI: 10.1002/(SICI)1097-4660(199701).

Tchobanoglous, G., Burton, F.L.,&Stensel, H.D. (2004). Wastewater Engineering Treatment and Reuse, 4<sup>th</sup> Edition, Mc Graw-Hill Seriesin Civil and Environmental Engineering, p1819.