

Adsorption Efficiency of Copper and Nickel by Activated Carbon from Coffee Ground

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Abstract

This study investigates the efficiency of coffee ground for copper and nickel adsorption. The coffee ground was carbonized at 700 °C and activated by sodium hydroxide (CGNa). The CGNa has many pores with varying sizes. Moreover, chemical bonds were broken during the carbonization and activation process. It composed mainly mesopores of 73%, Brunauer Emmett and Teller (BET) surface area of 274.02 m²/g, and average pore size diameters of 4.34 nm. The CGNa was used as adsorbent and it showed good adsorption efficiency for copper and nickel. Under pH 3 and 5 condition, the maximum adsorption capacity at equilibrium (qm) of copper and nickel was 2.09 mgCu/gCGNa and 1.04 mgNi/gCGNa, respectively. The optimum time for copper and nickel adsorption were determined at 5 minutes. The isotherm model which fits to experimental data was Langmuir model that shows monolayer coverage of copper and nickel on the sorption site of CGNa. As a result, utilization of coffee ground as an alternative activated carbon is useful to adsorb copper and nickel.

Keywords: Adsorption, Activation, Coffee Ground, Copper and Nickel

1. Introduction

Copper (Cu (II)) and nickel (Ni (II)) are usually detected in wastewater from electroplating industries, textile industries, leather manufacturing and dyeing (Dermentzis *et al.*, 2009), (Malkoc and Nuhoglu, 2006). The excessive levels of Cu and Ni in environment could be carcinogenic due to non-biodegradable and accumulated characteristic. Cu and Ni cause short and long term harmful effects even in small quantities. Therefore, elimination of Cu and Ni from aquatic ecology system is essential to protection environment and public health. The conventional treatment methods

for removal of Cu and Ni from wastewater are chemical precipitation, reverse osmosis, electro dialysis, ion-exchange, membrane filtration and adsorption. Compared to other methods, adsorption process has significantly high removal efficiency and low operation cost. Therefore, activated carbon is the most widely used as adsorbent. However, the cost of commercial activated carbon is relatively expensive. Thus, it is necessary to develop reasonable price of activated carbon specially gathering from low cost and abundant material. From previous research various agricultural waste (coconut coir pith, coffee ground, cashew nut shell, green tea waste, bagasse fly ash,

groundnut shells and sawdust) have been used for treatment of Cu and Ni from industrial wastewater (Kadirvelu, 2003; Laksaci *et al.*, 2017; Senthil Kumar *et al.* 2011; Shengxin *et al.*, 2016; Srivastava *et al.*, 2006; Shukla and Pai, 2005). Generally activated carbon should have high surface area, micro-porous structure, uniform pore size distribution, high porosity and strong adsorption capacity (Yingjie *et al.*, 2018). Fortunately, agricultural waste has a loose and porous structure. Moreover, contains carboxyl, hydroxyl, and other reactive groups. Therefore, it could be used as a biomass adsorption material in the field of pollution control, which can not only reduce the environmental burden but also achieve the effect of “treating waste by waste” (Huang, 2017). This research focus on the removal of Cu and Ni from aqueous solutions by coffee ground adsorption. The coffee ground is available waste from big city. In this research, coffee ground was prepared by carbonized at 700 °C and activated by sodium hydroxide (NaOH) to be CGNa. The chemical and physical characteristics of CGNa and the efficiency of Cu and Ni adsorption by CGNa were studied. Moreover, the effect of various experimental parameters such as solution pH, CGNa dose, contact time on the adsorption efficiency were investigated. Adsorption isotherm models were used to evaluate the experimental data and to illustrate the possible adsorption mechanism.

2. Materials and Methods

2.1 Chemicals and materials

All chemicals were analytical reagent (AR) grade for example Sodium hydroxide ($\geq 99.0\%$ purity), hydrochloric acid (37% purity), Ni 500 mL (Ni=1.000 \pm 0.002 g/L), Cu 500 mL (Cu=1.000 \pm 0.002 g/L) standards for Atomic Absorption Spectroscopy (AAS). Distilled water was used to prepare all of the solutions and reagents. The initial pH was adjusted by 0.1 M HCl and NaOH solutions. All the adsorption experiments were carried out in temperature control unit (25 ± 1 °C).

2.2 Preparation of activated coffee ground

The coffee ground was collected from a

coffee shop and then dried in the oven at 105 °C for 24 hours. The coffee ground was carbonized at 700 °C for 1 hour, to eliminate the volatile compounds and activated by sodium hydroxide (NaOH) at impregnation ratio of 1:1 (NaOH: char) (wt: wt) for 6 hours. Then the separated coffee ground from the liquid solution had been washed several times with boiled distilled water to remove any adhering dirt and color until pH was around 7. Then, the coffee ground was dried in the oven at 105 °C overnight and was carbonized at 700 °C for 3 hours. The final material was sieved in the size range of 200–300 mesh particle size and used as CGNa.

2.3 CGNa characterizations

The specific surface areas of CGNa were calculated using the BET (Brunauer Emmett and Teller) equation. The pore volume and pore size were determined by BJH method (Barrett-Joyner-Halenda) with Micromeritics, 3Flex Surface characterization, Georgia, USA. The determination of surface functional groups was done using a Fourier Transform Spectrophotometer model, BRUKER: Alpha-E. The scanning electron microscope (SEM) (Quanta 450 FEI, Hillsboro, OR, USA.) was used to characterize the adsorbent for constituent and morphology.

2.4 Adsorption experiments

The effect of initial concentration of adsorbate, pH, contact time, and adsorbent dose were studied by batch adsorption experiments. The adsorption experiments to determine the influence of pH were performed at various initial pH between 1-9 by HCl (0.1 M) or NaOH (0.1 M) adjustment. From the studies of Brigden *et al.*, 2010, wastewater from textile manufacturing facilities has a very high concentration of Cu and Ni at 20-300 mg/L. Thus, this research uses the initial concentration of 30 mg/L for Cu and Ni. The contaminated solutions were shaken at 200 rpm for 30 minutes under 25 °C. The studying of contact time was controlled as follows: 1 g of CGNa was mixed in 50 mL, the pH of solution was adjusted to 3 and 5. Then, the various contact times were at 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 45, 60, 90 and 120

minutes, respectively. The adsorbent dose was studied at range of 0.1-5 g at equilibrium contact time and suitable pH value. The solutions were filtered through a 0.45 μm glass fiber filter and measured their residual concentration by Atomic Absorption Spectrometer (AAS) operating with air-acetylene flame.

The Cu and Ni uptake (q) and Adsorption efficiency (AE) was calculated by the equation (1) and (2), respectively.

$$q \text{ (mg/g)} = \frac{(C_o - C_e)}{m} \times V \quad (1)$$

$$AE \text{ (%) } = \frac{(C_o - C_e)}{C_o} \times 100\% \quad (2)$$

C_o and C_e is the initial and the equilibrium concentrations of Cu or Ni (mg /L), respectively. V is the volume of the solution (L), and m is the mass of the adsorbent (g).

2.5 Adsorption isotherms

The adsorption equilibrium data were analyzed using the Langmuir and Freundlich adsorption isotherm models follow equation (3) and (4), respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m} (C_e) + \frac{1}{q_m} (K_L) \quad (3)$$

$$\ln q_e = \frac{1}{n} (\ln C_e) + \ln K_F \quad (4)$$

q_e (mg/g) is the amount of adsorbed Cu or Ni per weight unit of the adsorbent in equilibrium, C_e (mg/L) is equilibrium concentration of Cu or Ni in solution, q_m (mg/g) is the maximum monolayer adsorption capacity, K_F and K_L are the Freundlich and Langmuir adsorption coefficients, and n is the Freundlich exponent.

3. Results and Discussion

3.1. Pore structure characterization

The scanning electron microscopy (SEM) photos of CG and CGNa at 1000 magnification are presented in Fig. 1 (a) and (b). It clearly indicated the heterogeneous surface of CG and CGNa. The GC surface presents a few cracks on it without any apparent porous structure, while in Fig. 1 (b) the CGNa surface shows more damage with many cavities that indicate

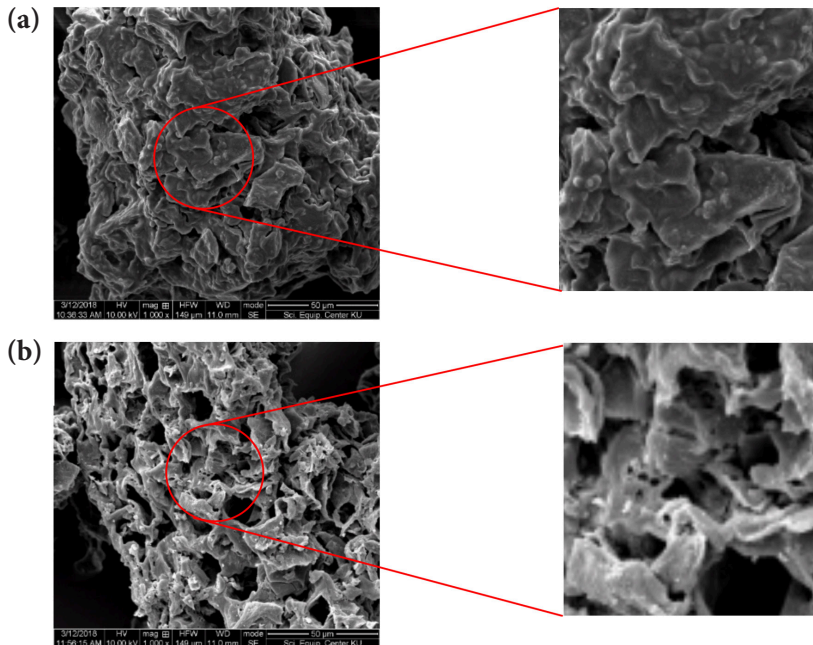


Figure 1. SEM images of (a) CG and (b) CGNa.

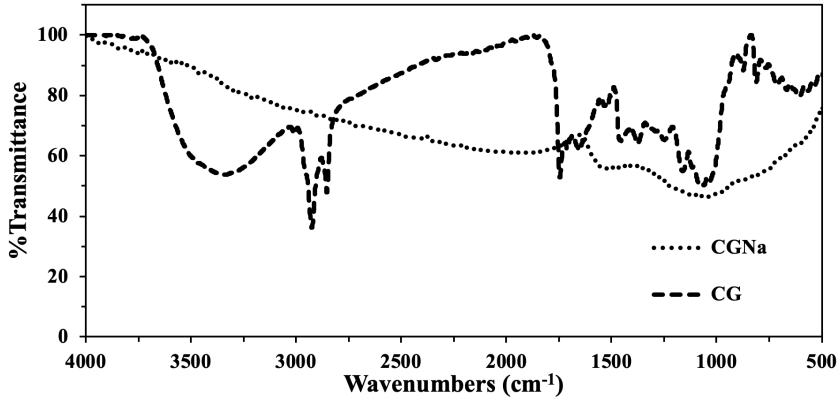


Figure 2. FTIR spectrum of CG and CGNa.

Table 1. Physical and pore characteristics from N₂ adsorption at 77 K experiment of CG and CGNa (Surface areas in m²/g, pore volumes in cm³/g and pore size in nm).

Sample	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)	Adsorption Pore Distribution (%)		
				Micropore	Mesopore	Macropore
CG	0.8574	-0.0003	7.9755	2.74	71.43	25.83
CGNa	274.0187	0.0816	4.3383	9.95	72.53	17.52

the development of pore structure after the activation process. The activation method with NaOH provides the development of many pores with varying sizes, increases surface area, and increases mesopore volume.

FTIR analysis results of CG and CGNa are showed in Fig 2. The FTIR spectra of CG demonstrate the presence of important functional groups. The bands located at 3329 cm⁻¹ correspond to bonded of O-H groups (alcohols, phenols, and carboxylic acids). The band at 2941, 2863 and 1738 and 1637 and 1139 and 1024 cm⁻¹ are assigned to C-H (alkane), C=O (carbonyl), C-C (aromatic) and C-O (alcohols, carboxylic acids, esters, and ethers), respectively. According to carbonization and activation of CGNa, some peaks were disappeared and several groups were shifted to different frequency. There was evidence of the disappearance of broad band at 3200–3600 cm⁻¹ and 1730-1740 cm⁻¹ correspond to the O-H and C=O functional groups, respectively. Therefore, O-H and C=O groups are the possible functional groups which involved to the interaction between coffee ground and effects of carbonization temperature followed

by activation with NaOH.

The important property of the adsorbent is its adsorptive capacity, which relate to the specific surface area. Table 1 shows the BET surface area of CG and CGNa at 0.86 and 274.02 m²/g, respectively. The pore size of most pores for CG and CGNa was almost larger than 2 nm with an average pore diameter of 7.97 and 4.34 nm, respectively, and the pore volumes were -0.0003 and 0.0816 cm³/g, respectively. As a result, using of NaOH as the activation reagent contribute to higher surface area of CGNa. There was also significant increase in mesopore and total pore volumes. The presence of mesopores (73%) in CGNa may be beneficial for its adsorption capacity. It has been well known that the mesopores facilitate the transfer of heavy metal ions (e.g., Cr, Cd, Pb, etc.) (Junting *et al.*, 2017). BET surface area is one of the most important characteristics of adsorbent material, because more adsorption sites would be available. The BET surface area of CGNa was high, indicating the suitability of activation procedure.

3.2 Effect of solution pH

The pH of the aqueous solution has important role in adsorption process since it influences not only the distribution of metal species in solution but also the surface properties of the adsorbents. As shown in the Fig. 3 (a) and (b), the adsorption percentage and adsorption capacity of Cu and Ni on the adsorbents CGNa increased with the increase of pH, indicating that pH has the strong influence on the adsorption. The maximum adsorption capacity of both adsorbents on Cu and Ni was obtained at pH 3 and 5, respectively, result in adsorption percentage of 84.84 and 62.50, respectively. Moreover, adsorption capacity of CG and CGNa is 0.92 mg/g and 0.72 mg/g, respectively. The results are similar to the previous studies of removal of Ni and Cu by nanocomposite of magnetic hydroxyapatite nanorods (Thanh *et al.*, 2018) and (Baes and Mesner 1998). It was expected that the precipitation of metal hydroxide occurred at

pH > 6.3 for $\text{Cu}(\text{OH})_2(\text{s})$ and pH > 8.3 for $\text{Ni}(\text{OH})_2(\text{s})$. Thus, the optimum pH for the removal of Cu and Ni by adsorption were fixed at 3 and 5, respectively for the next steps of the adsorption experiments.

3.3 Effect of adsorbent dosage

According to Fig 4 (a) and (b), the adsorption percentage of 30 mg/L of Cu and Ni (50 mL) are increased by increase of CGNa dosage. Cu adsorption percentage are shipped from 17.71 to 99.31 when the CGNa dosage are increase from 0.1 to 5 g, while the increasing from 9.86 to 79.56 adsorption percentage of Ni is occurred. On the other hand, adsorption capacity is decreased from 1.93 to 0.22 mg/g of Cu and 1.13 to 0.18 mg/g of Ni when the CGNa dosage is increase. The increasing adsorption percentage was detected due to the increase of adsorbent dose provides more sorption site (Liu *et al.*, 2014). Therefore, 1 g of CGNa was chosen as the optimum adsorbent dosage for the next

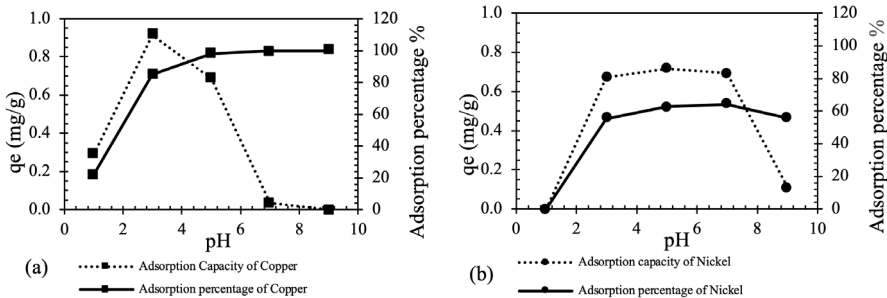


Figure 3. (a) and (b). Effect of initial pH on the adsorption of Cu and Ni on CGNa (Adsorbent dosage = 1 g, initial concentration = 30 mg/L, solution volume = 50 ml, temperature = 25 °C, contact time = 30 minutes).

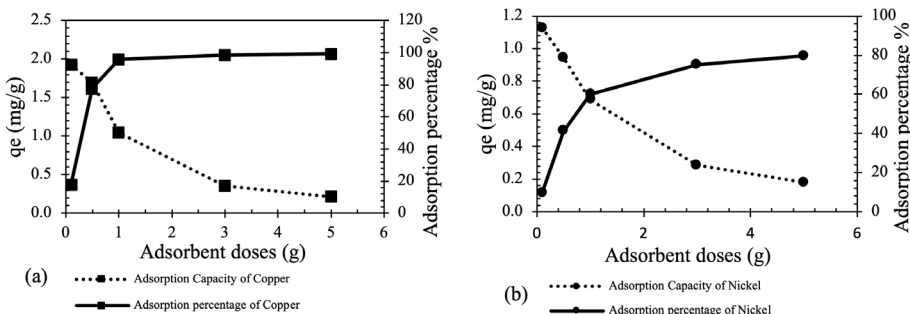


Figure 4. (a) and (b). Effect of adsorbent dosage on the removal of Cu and Ni (initial concentration = 30 mg/L, solution volume = 50 mL, pH = 3 and 5, respectively, temperature = 25 °C, contact time = 30 minutes).

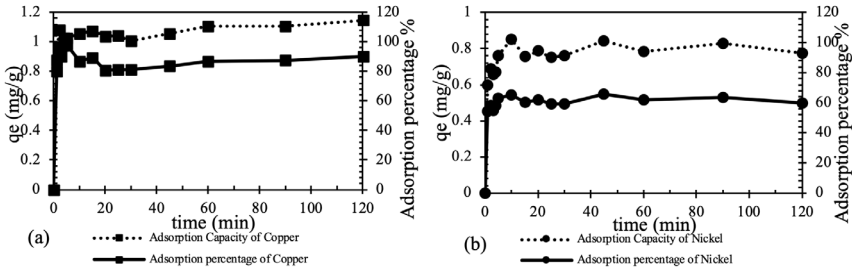


Figure 5. (a) and (b). Effect of contact time on the adsorption of Cu and Ni on CGNa (Adsorbent dosage = 1 g/50 mL, initial concentration = 30 mg/L, solution volume = 50 ml, temperature = 25 °C, contact time = 0–120 minutes).

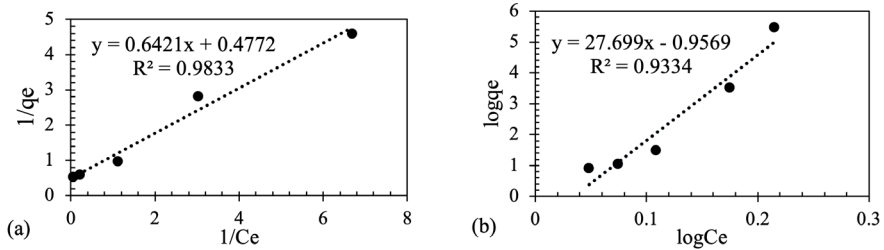


Figure 6. (a) and (b). Adsorption isotherm curve of Cu and Ni on CGNa using Langmuir isotherm model ($C_0 = 30$ mg/L, shaking time 5 minutes, adsorbent dose = 1 g/50mL, at pH 3 and 5 respectively and 25 °C).

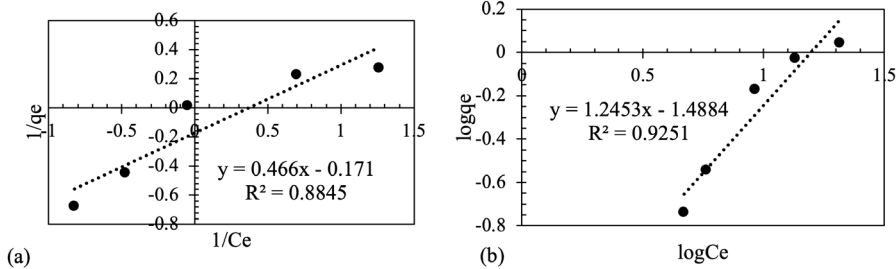


Figure 7. (a) and (b). Adsorption isotherm curve of Cu and Ni on CGNa using Freundlich isotherm model ($C_0 = 30$ mg/L, shaking time 5 minutes, adsorbent dose = 1 g/50mL, at pH 3 and 5 respectively and 25 °C).

experiments. This result is similar to the study of (Ridha and Hafiane, 2016) that small amount of 2 g MCWs was used as optimum dose to adsorb methyl orange (MO) with 99% adsorption. 50 ml of the dye solution (50 mg/L).

3.4 Effect of contact time

The influence of contact time (1–120 minutes) on Cu and Ni studied at initial concentration 30 mg/L and 1 g adsorbent dose. The results are demonstrated in Fig. 5 (a) and (b). The rapid sorption was obtained within the first 5 minutes where the instantaneous

adsorption or external surface adsorption occurred. Thereafter, the adsorption rate became practically constant until 120 minutes. The optimum equilibrium contact time of Cu and Ni adsorption reached equilibrium within 20 and 5 minutes, with adsorption efficiency of 80.19 % and 61.88 %. The adsorption capacity is 1.09 mg/g and 0.68 mg/g for Cu and Ni adsorption, respectively. The sorption of Cu and Ni was constant, when the increase of contact time, which is depend on the decrease in the number of sorption sites on the surface of CGNa. Therefore, the adsorption involves a

Table 2. Parameters of adsorption isotherms of Cu and Ni on CGNa at 25 °C.

Heavy Metal	Langmuir Isotherm			Freundlich Isotherm		
	q_m	K_L	R^2	K_F	$1/n$	R^2
Ni	1.05	26.51	0.9334	0.0325	0.8030	0.9251
Cu	2.10	0.31	0.9833	0.6745	2.1459	0.8845

surface reaction process. The initial adsorption is rapid. Then, as lower adsorption would follow, as the available adsorption site gradually decreases, which is consistent with studies reported before (Wang *et al.*, 2008), (Mezener and Bensmaili, 2009).

3.5 Adsorption isotherms

Langmuir and Freundlich isotherm models were applied to study the adsorption behavior and to determine the adsorption capacity of CGNa on Cu and Ni. The isotherm experiment reveals well fit with Langmuir isotherm (Fig. 6 (a) and (b)), but the application of the empirical Freundlich isotherm were less satisfactory results (Fig. 7 (a) and (b)). The values of the adsorption and the correlation coefficients are given in Table 2. The linearity of Langmuir plots for Cu and Ni (correlation coefficients $R^2 > 0.98$, 0.93 , respectively) suggests strong bonding involving chemical forces between Cu and Ni and CGNa particles. The results suggested that, the mechanism of Cu and Ni uptake is homogeneous adsorption process and showed monolayer coverage of Cu and Ni on the CGNa adsorbent surface. Based on Langmuir isotherm, the maximum adsorption capacity (q_m) of Cu and Ni was estimated to be 2.09 mg/g and 1.04 mg/g, respectively.

4. Conclusions

Thus, this research demonstrated that coffee ground can be exploited as the good adsorbent material for Cu and Ni at initial concentration of 30 mg/L. The optimum pH for the adsorption of Cu and Ni were 3 and 5, respectively. Within short contact time of 5 minutes, it can remove more than 80% of Cu and 62% of Ni. The optimum adsorbent doses were 1 g of CGNa. The adsorption isotherm of Cu and Ni on CGNa are well fit to Langmuir

model. Moreover, it confirmed homogeneous adsorption process and showed monolayer coverage of Cu and Ni onto the CGNa adsorbent surface. The results indicate that coffee grounds may be used as an inexpensive, effective and easily used as adsorbent for the removal of Cu and Ni from aqueous solutions.

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