

Application of Rubber Wood Ash for Removal Nickel and Copper from Aqueous Solution

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Abstract

The attempt of this study was to use rubber wood ash (RWA), an agricultural waste, as an adsorbent for the adsorption of Ni(II) and Cu(II) ions from aqueous solution. The average particle size of RWA was 35.4 μm . The BET surface area was 42 m^2/g . SEM of RWA reveals it very fine particle size to the order of millimeter or less and that there are pores of varying sizes within the particle. The diffraction pattern confirms the CaO is the main content in RWA. Studies were carried out on the function of rotation speed, amount of dosage and contact times. RWA was found to be an effective adsorbent for the removal of 99.86% for nickel (Ni(II)) and 99.44% for copper (Cu(II)) metal ions from aqueous solutions. Optimum conditions for Ni(II) and Cu(II) ions removal were found to be adsorbent dosage of 10 g/l, 20 minutes equilibrium time and rotation speed of 400 rpm. The results suggest that RWA can be used as an adsorbent for an efficient removal of metal ions from aqueous solutions.

Key words: Adsorption/ Heavy metal/ Removal/ Rubber wood ash (RWA)

1. Introduction

The presence of heavy metals in aqueous water streams has become a problem due to their harmful effects on human health. It is recognized that finding methods for removal of heavy metals from aqueous water is of great importance. Nickel and copper are among the heavy metals affecting the environment.

Nickel and copper, are element which have been widely used in many products for consumer, industrial,

military, transport/aerospace, marine and architectural applications. However, these can be regarded as a longstanding environmental contaminant. Nickel is also a common environmental pollutant and is toxic (e.g. in concentrations more than 15 mg/l), especially to activated sludge bacteria, and its presence is detrimental to the operation of anaerobic digesters used in wastewater treatment plants (Patterson, 1977). It has been reported that excessive intake of copper by humans may lead to severe mucosal irritation, hepatic and

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renal damage, capillary damage, gastrointestinal irritation and central nervous system irritation (Larous et al., 2005). Nickel and copper can be removed by precipitation as nickel and copper hydroxide but this method is only efficient at high pH value. Other conventional methods which have been employed to remove nickel and copper in wastewater include ion-exchange, membrane separation, electrochemical treatment, reverse osmosis and solvent extraction (Cheung et al., 1997). All these methods are generally expensive; therefore it is important to search for a low-cost method which is effective and economic. The adsorption technique is much preferred for removal of heavy metals because of its efficiency and low cost. The use of activated carbon (AC) as an adsorbent has now been regarded as a major process for wastewater treatment. However, due to high cost and about 10–15% loss during AC regeneration, non-conventional and cheap adsorbents like waste tea leaves (Tee et al., 1998), sago waste (Quek et al., 1998), peanut hulls (Brown et al., 2000), hazel nut shell (Cimino et al., 2000), saw dust (Sukla et al., 2002), neem bark (Naiya et al., 2008), chitin beads (Zhou et al., 2004), thermally treated rice husk ash (Doner et al., 2004), waste banana, orange peels (Annadurai et

al., 2003), cocoa shells (Meunier et al., 2003), tree fern (Ho et al., 2003), coffee residue (Boonamnuayvitaya et al., 2004), rice husk (Chuah et al., 2005; Feng et al., 2004), palm kernel fibre (Ho et al., 2005), olive stone waste (Fiol et al., 2006), grape stalk (Martinez et al., 2006), coir (Quek et al., 1998; Conrad et al., 2007), tea waste (Amarasinghe et al., 2007), bagasse fly ash (Gupta et al., 1998; Gupta et al., 2004), etc. have been all used as alternative adsorbents.

Rubber wood is wood from the Pará rubber tree (*Hevea brasiliensis*). There are extensive plantations with these trees in Southeast Asia. For instance, the traditional practice was to burn the tree at the end of its latex-producing cycle. Rubber wood is used only after it completes its latex producing cycle, generally when it is 25-30 years old. When the latex yields become extremely low, the trees are then felled, and new ones are usually planted. It can also be used as fuel, either in a furnace, generator, or with steam for boiler power. It may also be smelted into charcoal, with that fuel being used where appropriate. Rubber wood ash (RWA) is an abundant agricultural waste, accounting for about of the annual gross rubber wood ash, 217 million metric tons of the annual gross waste in Thailand (Office of agricultural

economics, Thailand, 2013). Due to growing concern about environmental pollution, and the need to conserve energy and resources, efforts have been made to burn rubber wood under controlled temperatures and atmospheres as a supplementary cement material.

The main purpose of this paper is to study the removal of nickel and copper ions by using adsorption and to determine the ability of RWA to remove of nickel and copper ions from aqueous solution. Also effects of adsorbent dosage, contact time and the rotation speed variation are investigated.

2. Experimental

The chemical reagents used in the experiments were of analytical grade. Aqueous solutions of Ni(II) and Cu(II) ions were prepared from $\text{Ni}(\text{NO}_3)_2$ and $\text{CH}_3\text{COO}_2\text{Cu}$, respectively. Deionized water was used throughout the study.

2.1. Rubber wood ash treatment and analysis

Rubber wood ash is a by-product generally obtained from steam boiler and a solid obtained after the burning of rubber wood. The morphology of RWA particles was investigated with a scanning electron microscope (SEM; JEOL JSM-

5800LV). Particle size distribution of RWA was characterized by Beckman Coulter (Mastersizer 2000 Version 5.1). The specific surface area of the adsorbent was determined by Brunauer-Emmett-Teller (BET) method. X-ray fluorescence (XRF) analysis was carried out to determine chemical compositions of RWA. The RWA was supplied by the Songkhla region (South of Thailand). Samples of RWA were heated at a temperature of 500°C with the holding time of 1 hour under a heating rate of $10^\circ\text{C}/\text{min}$.

2.2. Batch adsorption experiment

A 100 ml of solution was added to the beaker containing the desired adsorbent. At the end of predetermined time intervals, the concentration of Ni (II) and Cu(II) was determined. All experiments were carried out three times and the adsorbed nickel and copper ions concentrations given were the means of duplicate experimental results. Experimental variables considered were initial concentration of Ni(II) and Cu(II) 50 mg/l; contact time between RWA with Ni(II) and Cu(II) ion solution 5–25 min; dosage of RWA was between 0.6-1.2 g/100 ml. Inductively coupled plasma atomic emission spectrometer (ICP-AES) was used for the analysis of Ni(II) and

Cu(II) in aqueous solution. An aqueous solution of nickel and copper ions (the concentration of solution was 50 mg/l), rotation time was 15 min and the amount of RWA 1 g/100 ml were used to study the effect of rotation speed on the sorption. The pH value of the aqueous solution was 7. In previous study (Vimal et al., 2006, Mohsen et al., 2011), modification to pH value was 7 for selected as an optimized value for further adsorption studies. The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization and speciation of different pollutants (Elliott and Huang 1981). The experiment was carried out at room temperature to investigate the efficiency of the sorbents for removing heavy metals.

The percentage removal of metal ions and equilibrium adsorption uptake in solid phase, were calculated using the following relationships:

$$\text{Percentage metal ions removal} = \frac{100(C_0 - C_e)}{C_0} \quad (1)$$

Where, C_0 is the initial metal ion concentration (mg/l), C_e is the equilibrium metal ion concentration (mg/l).

3. Results and discussion

3.1 Properties of RWA

SEM micrographs of the RWA indicated that the surface was highly irregular and porous in nature is shown in (Figure 1) reveals its surface texture and porosity. It shows very fine particle size to the order of a millimeter or less and that there are pores of varying sizes within the particle, RWA has high porosity and thereby high surface area (42 m²/g (Table 1)). Chemical composition of RWA is 48.24%CaO was found to be the main content in RWA (Table 1). The particle size distributions generated were characterized using D_{50} , which is the 50% passing size in the cumulative distribution. The particle size distribution in Figure 2 shows that the original RWA presents a reasonably wide range of particle sizes, the RWA present values of D_{50} between 35.4 μm .

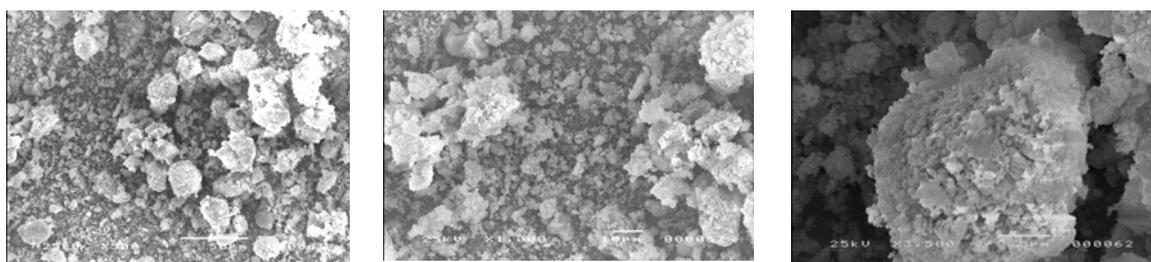
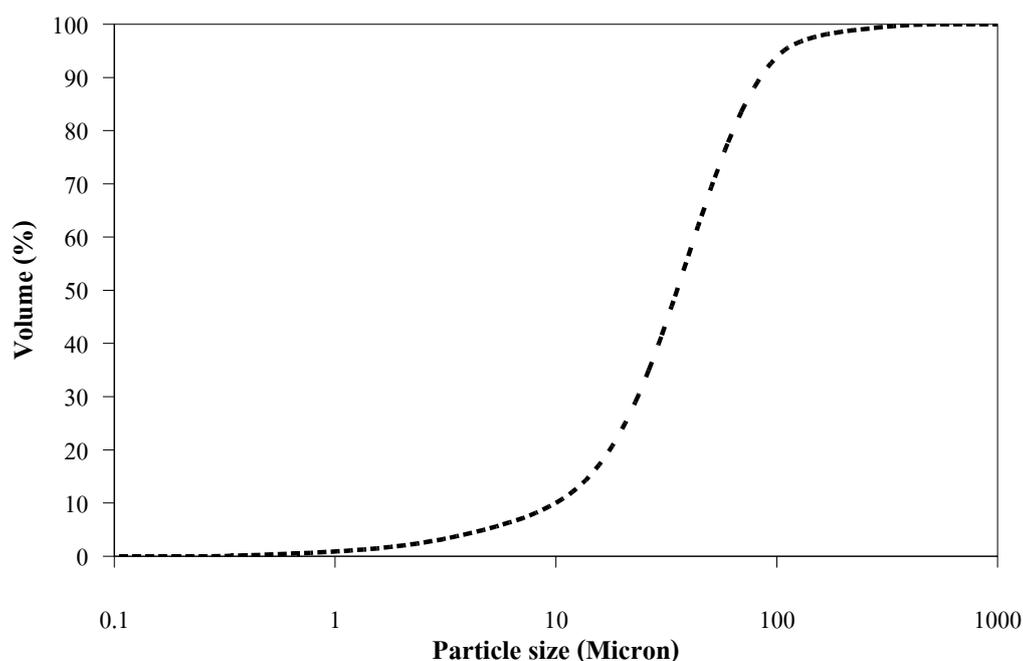


Figure 1: SEM Images of RWA at 500X (left), 1000X (middle) and 3500X (right).

Table 1: The chemical compositions (%) with X-ray fluorescence analysis and some properties of RWA

CaO	SiO ₂	K ₂ O	MgO	P ₂ O ₅	SO ₃	Al ₂ O ₃	Fe ₂ O ₃	MnO ₂	Cl	SrO	LOI*
48.24	1.52	8.44	3.50	1.86	1.28	0.26	0.26	1.42	0.30	0.10	32.82
Specific surface area: 42 m ² /g											
* LOI – loss on ignition.											

**Figure 2:** Particle size distribution of the RWA.

3.2 Influence of rotation speed

The rotation speed of the magnetic mixer for the sorption of nickel and copper ions onto sorbent was optimized at the range of 200 to 600 rpm. The results are shown in Figure 3. The removal of nickel and copper ions increases with every increment in the rotation speed up to 400 rpm, thereafter a decrease is observed. The decrease in sorption of nickel and copper ions at very high speed

may be due to the over agitation of the sorbate ions in the sorption vessel, as a result repulsion forces predominate on the sorptive sites on the sorbent surface, which ultimately reduce the attraction between sorbate and sorbent (Blinova et al., 2007). Therefore, 400 rpm was selected as an optimized rotation speed for further sorption studies.

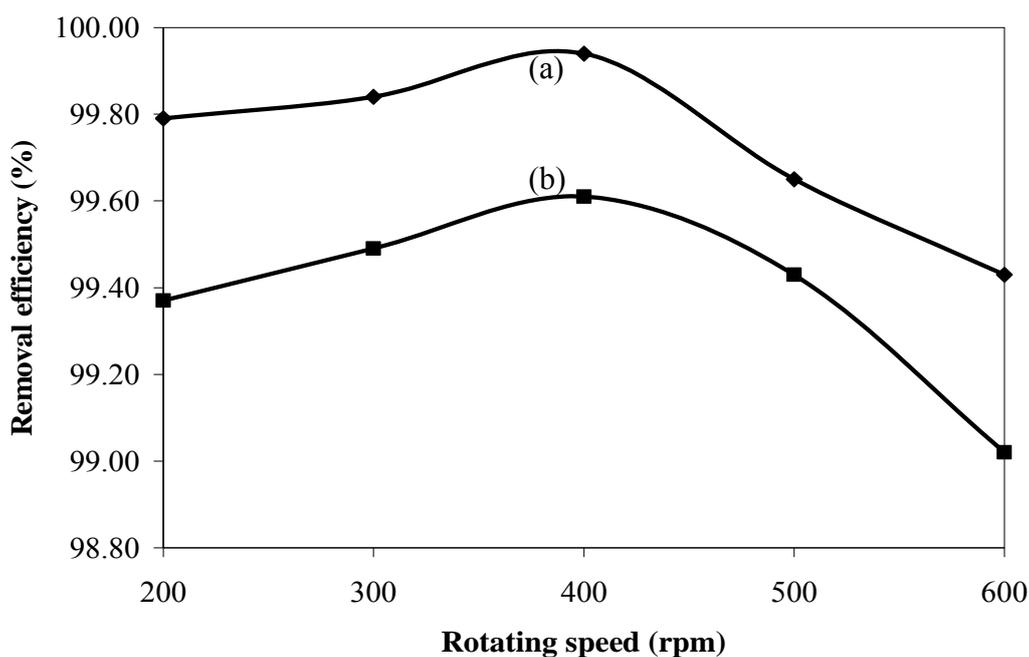


Figure 3: The effect of rotation speed on the removal efficiency of: (a) Ni(II) and (b) Cu(II) (with the initial concentration, pH, contact time, volume of solution and amount of adsorbent was 50 mg/l, 7, 15 min, 100 ml and 1 g, respectively).

3.3 Influence of sorbent dosage

The removal percentage of nickel and copper ions was studied by varying the adsorbent (RWA) dose between 0.6, 0.8, 1.0 and 1.2 g with a nickel and copper ions concentration of 50 mg/l. Results are presented in Figure 4. This figure reveals that the removal of metal ions increases with increase in adsorbent dosage from 0.6 to 1 g/100 ml. The removal remains unchanged above 1 g/100 ml of RWA dosage. An increase in the adsorption with the adsorbent dosage can be attributed to the availability of greater surface area and more adsorption sites. At sorbent dosage less than 1 g/100 ml, the adsorbent surface becomes

saturated with metal ions and the residual metal ion concentration in the solution is large. With an increase in adsorbent dosage, the metal ions removal increases due to increased metal ions uptake by the increased amount of adsorbent. At sorbent dosage more than 1 g/100 ml, the incremental metal ions removal becomes very low, as the surface metal ions concentration and the solution metal ion concentration come to equilibrium with each other. At about sorbent dosage 1 g/100 ml, the removal efficiency becomes almost constant. Maximum removal of metal cations at $C_0 = 50$ mg/l was found to be 99.8% for Ni(II) and 99.4% for Cu(II).

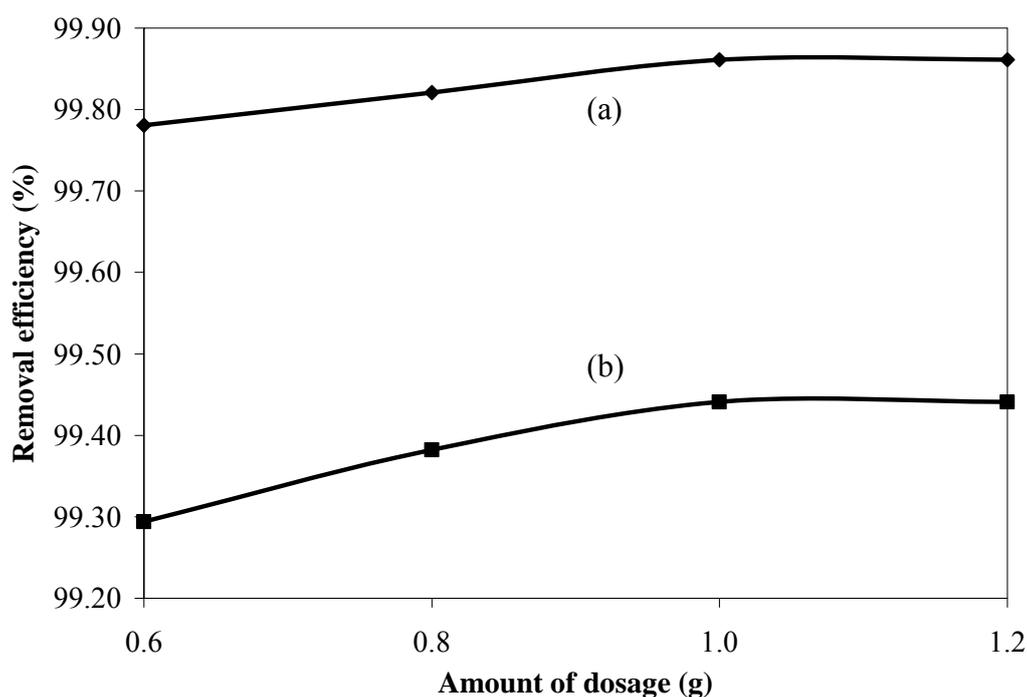


Figure 4: The effect of adsorbent dosage on the removal efficiency of: (a) Ni(II) and (b) Cu(II) (the initial concentration, rotation speed, pH, contact time and volume of solution was 50 mg/L, 400 rpm, 7, 15 min and 100 ml, respectively).

3.4 Effect of contact time

Figure 5 shows the effect of contact time on sorption of nickel and copper ions by RWA. For these cases, initial nickel and copper ions concentration was 50 mg/l and pH of 7 was used for nickel and copper solution. Also RWA dose of 1 g added in 100 ml. For Ni(II) and Cu(II) sorption rate reaches up to 99.86% and 99.44%, respectively, at 20 min, after which very little sorption was observed. This result revealed that adsorption of nickel and copper was fast and the equilibrium point was achieved after 20 min of contact time. Taking into account these results, a contact time of 20 min was chosen for further experiments.

The removal of metal ions could, therefore, be the net result of the “ion exchange” and “surface complexation” phenomena occurring on the surface (Khalid et al., 1998). The removal of the cations was in the order: Ni(II) > Cu(II) (Figure 4). The trend is according to decreasing size of the ionic radius: Ni(II) (0.69) < Cu(II) (0.71) (Susete et al., 2000, Vimal et al., 2006, Afsaneh et al., 2011). Smaller size metal ions could get adsorbed more deeply into pores big enough not to adsorb much greater size metal ions. Since RWA is predominantly porous, most of the cations get adsorbed into pores (Figure 1).

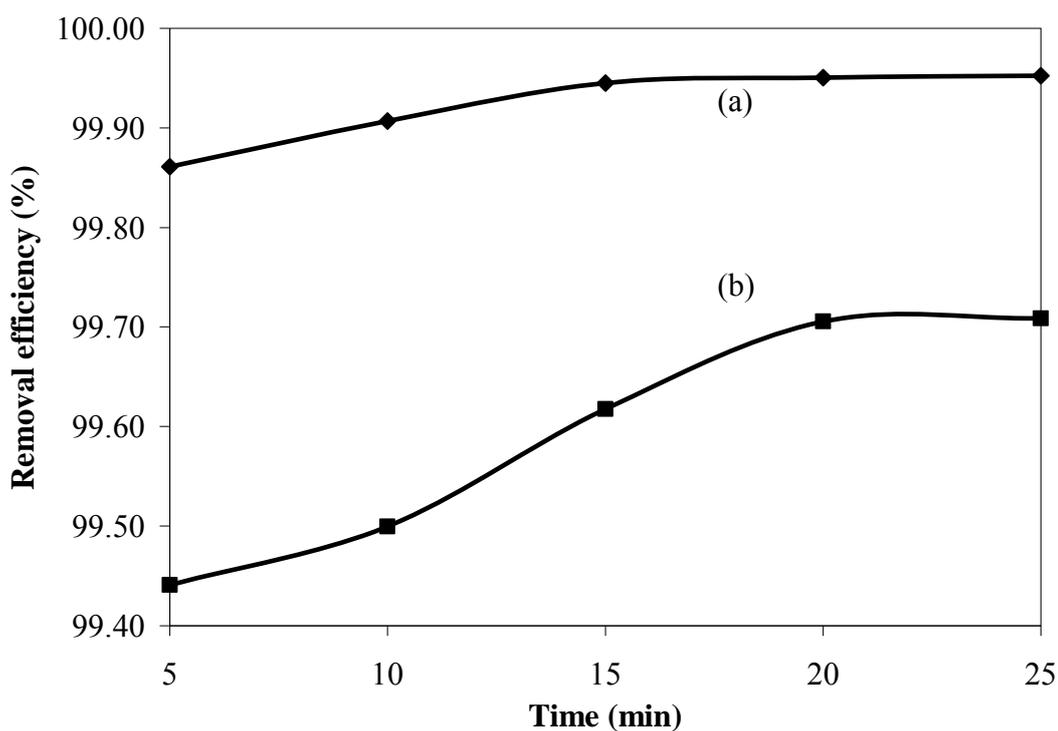


Figure 5: The effect of contact time on the removal efficiency of: (a) Ni(II) and (b) Cu(II) (the initial concentration, rotation speed, pH, volume of solution and amount of adsorbent was 50 mg/l, 400 rpm, 7, 100 ml and 1 g, respectively).

4. Conclusions

It can be summarized that as an agricultural waste, rubber wood ash, was found to be a suitable adsorbent for the adsorption of nickel and copper ions from aqueous water. Equilibrium between the metal ions in the solution and on the RWA surface was practically in 20 minutes and rotation rate 400 rpm. Maximum metal ions removal at $C_0 = 50$ mg/l at 10 g/l adsorbent dosage is found to be 99.86% for Ni(II) and 99.44% for Cu(II). The adsorption capability of

RWA for nickel and copper ions is considerably higher and faster, respectively, than many other methods.

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