Waste tire rubber as heavy metal ion adsorbent

P Boongoi1,2, M Opaprakasit1,2 and O Boondamnoen1,2,*

1 Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
2 Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok 10330, Thailand

*Corresponding Author’s E-mail: orathai.b@chula.ac.th

Abstract. The objective of this work was to develop waste tire rubber (WTR) as a heavy metal ion (Cu(II)) adsorbent. Effects of heat and acid treatment on efficiency of Cu(II) removal were examined from h-WTR, a-WTR, h/a-WTR and a/h-WTR with 40 mesh size. Results from UV-Vis spectrometer revealed that, at 0.5g/50ml adsorbent dosage, h-WTR had higher %removal of Cu(II) than other treated-WTRs. This may result from the highest surface area (51.61 m²/g) and pore volume (0.24 cm³/g) of h-WTR. The pores were possibly formed by the departure of small compounds generated from the rubber degradation. On the other hand, acid treated adsorbent present low efficiency, positive charges of the residual acid occupied on adsorbent surfaces played an important role on the Cu(II) adsorption capacity of a-WTR, h/a-WTR. SEM image presented the number of pores on surface of h-WTR. Results from h-WTR with different size revealed that the smaller size of WTR provided the higher %removal of Cu(II). This was possibly due to the higher efficiency of surface activation. Increasing an amount of adsorbent dosage from 0.5 to 5g/50ml slightly enhanced the %removal. In this study, WTR with > 90% Cu(II) removal was achieved when heat treatment was applied on 40 mesh WTR and 0.5g/50ml adsorbent dosage.

1. Introduction

Heavy metal in wastewater is one of the major concerns because it is toxic to environment and human health. It cannot be decomposed by natural processes, moreover, it is stable and accumulate in air, soil, water, bodies and organism. Copper (II) ion (Cu(II)) is one of the most harmful heavy metal. It was widely found in industrial wastewater from metal process, mining, electronics circuit, and textile. The maximum allowable contaminant levels of copper issued by Environmental Protection Agency (EPA) is 1.3 mg/l [1]. The accumulation of Cu (II) in body can cause gastrointestinal irritation, damage liver and lung cancer [2]. Therefore, it is very important to control the amount of Cu(II) in permissible limit before discharge to environment. The conventional methods of wastewater treatment are precipitation, coagulation, filtration, ion exchange resins, solvent extraction and adsorption [3,4]. Adsorption is the extensively used technique because it presents higher efficiency, simple design and lower investment compared of other techniques [5,6]. Activated carbon is carbonaceous adsorbent that possesses high capacity of adsorption due to its high surface area and pore volume [7]. However, it has many disadvantages which are high commercial cost and imported from abroad. Various carbonaceous adsorbents derived from natural materials [8], graphite [9] and waste tire rubber (WTR) have been researched for wastewater treatment. WTR is interesting because the number of waste tires increases many billion tons per year [10]. Disposal of this kind of waste has become major challenges because
WTR has highly complex structure and various compositions. It is considered as thermoset which is hard to degrade in normal condition. WTR was used in various applications to manage unused tires such as asphalt pavements, concrete, plastic composites and solid fuels [11,12]. In addition, WTR contains up to 70-75% carbon component [13] which is good enough to be used as carbon source for carbonization and possibly develop as heavy metal adsorbent. Therefore, the benefit of using this kind of waste is not only to separate heavy metal ion from wastewater but also to reduce its impact on environment issue. In this work waste tire rubber is selected as an adsorbent for removing Cu(II) from aqueous media.

High surface area and pore volume are principal properties required for adsorptive materials. In addition, active sites on the surface possibly enhance adhesion between heavy metal ions and adsorbents. Heat treatment in limited oxygen is interesting method because it could increase surface area and pore volume of materials. In addition, the interaction on surface of adsorbent could be developed by acid or basic treatment [7]. Treating with sulfuric acid (H₂SO₄) has been reported as one of the successful methods [14]. It produces porosity and sulfonic acid on surface of WTR, hence its adsorption mechanisms are though physical and chemical adsorption [15]. Therefore, this work aimed to investigate feasibility of developing the high-efficiency adsorbent from WTR. The study was conducted by treating WTR with difference methods, i.e., heat treatment, acid treatment and the combination of heat and acid treatments (2-step treatments). It was speculated that sequentially treating WTR with heat and acid (or vice versa) possibly synergized effects of each treatment. Effect of WTR size on the efficiency of treatment was verified with heat treatment process. Moreover, dosage of the developed adsorbents on the capacity of % Cu(II) removal was investigated as well. Surface area, pore volume and surface morphology were characterized by BET and SEM.

2. Experimental Procedure
2.1. Materials and chemicals
WTR with 10 and 40 mesh sizes was purchased from Union commercial development Co., Ltd. (Thailand). Copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) (99.5% from Qrec, New Zealand), hydrochloric acid (HCl), sodium hydroxide (NaOH), and sulfuric acid (H₂SO₄) (98% pure, RCI Labscan Limited) were supplied in analytical grade.

2.2. Preparation of adsorbent from WTR
Heat treatment, acid treatment and two step treatment were carried out for developing adsorbent from WTR (table 1). For heat treated WTR (h-WTR), WTR was heated at 2°C/min in a furnace with limited oxygen atmosphere. h-WTR was obtained after isothermally heating at 400°C for 2 h. Effect of WTR mesh size (10 and 40) on treatment efficiency was verified using the heat treatment approach. For acid treated WTR (a-WTR), WTR with 40 mesh size was impregnated in 70 wt% H₂SO₄ solution using the ratio of WTR to H₂SO₄ at 1g:7ml. Then, it was stirred continuously with agitation rate at 240 rpm for 4 h and further soaked overnight. a-WTR was received by filtering and neutralizing with distilled water. a-WTR was dried in an oven at 95°C for 2 h for further uses. For two-step treated WTRs, a/h-WTR and h/a-WTR were prepared. While h/a-WTR was obtained by subsequently impregnating h-WTR in 70 wt% H₂SO₄ solution, a/h-WTR was prepared by further heat treating a-WTR at 400°C for 2 h in a furnace.

| No | Name     | Treatment method | Conditions (temp (°C)/acid aq.) |
|----|----------|------------------|-------------------------------|
| 1  | WTR      | No treatment     | -                             |
| 2  | h-WTR    | Heat treatment   | 400                           |
| 3  | a-WTR    | Acid treatment   | H₂SO₄                         |
| 4  | h/a-WTR  | Heat/Acid        | 400/ H₂SO₄                    |
| 5  | a/h-WTR  | Acid/Heat        | H₂SO₄/400                     |
2.3. Adsorption of Cu(II)
Cu(II) solution was prepared by dissolving 1.2 g of Cu(NO$_3$)$_2$·3H$_2$O in 1000 ml of deionized water. Its initial concentration ($C_0$) was measured by UV-Vis spectroscopy (UV-Vis, Blue star B, S/N: 1812UV1790, Lab tech). 0.5 and 5.0 g of treated-WTR were added to 50 ml of Cu(II) solution. Then pH of the solution was adjusted to 6 using 0.1 mol/L HCl and 0.1 mol/L NaOH. After the mixture was stirred at 700 rpm for 10 min and at 250 rpm for 50 min at room temperature, the adsorbent was filtered. The residual concentration of Cu(II) in filtrate was evaluated using UV-Vis spectrophotometer. %removal of Cu(II) was calculated according to equation 1.

$$\%\text{Adsorption} = \frac{C_0 - C_e}{C_0} \times 100$$

(1)

Where $C_0 = \text{Initial heavy metal concentrations in solution (mol/L)}$
$C_e = \text{final heavy metal concentrations in solution (mol/L)}$

2.4. Thermal degradation
The degradation of untreated WTR was studied by thermogravimetric analysis (TGA/SDTA, Metler Toledo). The sample was heated up from 35 to 650°C under N$_2$ atmosphere. The heating rate was fixed at 10°C/min.

2.5. Textural properties
The specific surface area ($S_{\text{BET}}$) and pore volumes ($V_{\text{TOT}}$) of all adsorbents were investigated by gas adsorption-desorption (N$_2$), using Brunauer Emmette-Teller technique (BET, 3flex surface characterization, Micromeritics). The surface morphology of untreated and treated WTRs were examined by Scanning Electron Microscope (SEM, JEOL JSM-6480LV).

3. Results and Discussion
The capacity of Cu(II) removal of all treated-WTR were presented in figure 1. The untreated WTRs showed the lowest %Cu(II) adsorption at less than 10%. Smaller size of WTR presented no improvement of the removal efficiency. In contrast, h-WTRs had much better efficiency than WTR. Moreover, %adsorption of 40 mesh h-WTR was ~30% higher than that of 10 mesh h-WTR. Result of thermal decomposition of WTR investigated by TGA was shown in figure 2. WTR dramatically degraded in the temperature range of 340 - 460°C. The highest degradation rate was at 385°C at which the peak of DTG was seen. At temperature higher than 460°C, no mass loss of WTR was further observed and rigid char was formed. It had been reported that small molecules of N$_2$, H$_2$, CH$_4$, NH$_3$, etc. were possibly formed and released out during WTR decomposition [7, 11]. Finally, the gummy char, porous amorphous carbon skeleton structure resulted from carbon black, solid hydrocarbon and other inorganic compounds, was remained [7,16]. This implied that h-WTR structure was likely similar to the reported gummy char. This provided the explanations why %adsorption, $S_{\text{BET}}$ and $V_{\text{TOT}}$ of h-WTR (table 2) were much higher than those of WTR. It was believed that Cu(II) from aqueous medium diffused and then adhered on surface of h-WTR by physical adhesion. Therefore, the adsorption of Cu(II) on this adsorbent increases when surface area and pore were increased. By comparing results of 2 different dosages, % Cu (II) removal of 0.5 g h-WTR was not much different from that of 5.0 g h-WTR. Typically, the higher content of adsorbent should provide higher surface area for metal binding. However, this obviously was not in good agreement with the results of 10 mesh h-WTR. The total surface area, active in Cu(II) adsorption, of 0.5 g h-WTR seemed comparable to 5 g h-WTR. This implied that at high dosage, the reduction of interparticle distances between adsorbent particles and the particle agglomeration possibly hindered accessibility of metal ions to the absorbent’s active surface [17]. Moreover, increasing dosage of a-WTR imposed the adverse effect on Cu(II) adsorption efficiency. This result was additionally caused by residual positive charges remained on a-WTR after acid treatment. The reduction of %adsorption at higher a-WTR dosage was likely resulted from repulsive forces between those positive charges and
Cu(II) and their limited accessibility of Cu(II) to active sites on a-WTR. From these results, 0.5 g dosage was interested and chosen for further study.

![Figure 1](image1.png)

**Figure 1.** % removal of Cu(II) using different types of adsorbents at 10 and 40 mesh size, and 0.5 and 5 g dosage.

![Figure 2](image2.png)

**Figure 2.** TGA and DTG thermographs of WTR.

| Adsorbent | Size (mesh) | Textural properties |
|-----------|-------------|---------------------|
|           | 10  | 40 | $S_{\text{BET}}$ (m$^2$/g) | $V_{\text{TOT}}$ (cm$^3$/g) |
| WTR       | ✓   |   | -             | -             |
| h-WTR     | ✓   |   | 0.44          | 0.38x10$^{-3}$|
| a-WTR     | ✓   |   | 51.61         | 0.24          |
| h/a-WTR   | ✓   |   | 0.11          | 0.55x10$^{-4}$|
| a/h-WTR   | ✓   |   | 0.32          | 0.34x10$^{-3}$|

**Table 2.** The surface area ($S_{\text{BET}}$) and pore volume ($V_{\text{TOT}}$) of different adsorbents.
Among 4 types of treated WTRs, results in figure 3 showed that efficiency of Cu(II) adsorption decreased as follows: h-WTR, a/h-WTR >> h/a-WTR > a-WTR > WTR. %adsorption of a-WTR was about 3X-6X as high as that of the untreated WTR, however, the acid treatment was not as powerful as heat treatment. In addition, incorporating acid treatment into 2 step methods made efficiency of h/a-WTR markedly worse than h-WTR. Therefore, it was suspected that the porous structure previously formed in heat treatment was possibly damaged when acid treatment was subsequently carried out [18].

%adsorption of a/h-WTR was also slightly lower than h-WTR. These results were in good agreement with their \( S_{\text{BET}} \) and \( V_{\text{TOT}} \) values. From table 2, \( S_{\text{BET}} \) and \( V_{\text{TOT}} \) values of h-WTR and a/h-WTR were obviously higher than those of WTR, a-WTR and h/aWTR. While \( S_{\text{BET}} \) and \( V_{\text{TOT}} \) of h-WTR and a/h-WTR were 52 – 56 m\(^2\)/g and 0.15 - 0.24 cm\(^3\)/g respectively, those of a-WTR and h/a-WTR were 0.11-0.32 m\(^2\)/g and 0.5 \( \times 10^{-4} \) – 0.3 \( \times 10^{-3} \) cm\(^3\)/g. Moreover, it was evident that pH of the residual Cu(II) solution was 5 when a-WTR and h/a-WTR were used. But the residual Cu(II) solution remained at 6 for h-WTR and a/h-WTR. This possibly implied that positive charges left on the surface of adsorbents after acid treatment impaired the Cu(II) absorptivity of treated WTR [10].

**Figure 3.** % removal of Cu(II) of adsorbents prepared from different methods at 40 mesh size and 0.5 g dosage.

SEM micrographs of WTR, a-WTR and h-WTR were shown in figure 4. It clearly showed that surface of WTR was smooth with few voids. In contrast, rough surfaces resulted from acid and heat treatment were observed from a-WTR (figure 4b) and h-WTR (figure 4c). Etched surface of a-WTR contained large-scale features. A lot of tiny pores on h-WTR surface were possibly produced during the vaporization process of volatile products of heat treatment. It could be concluded that heat-treated WTR has potential for utilization as a Cu (II) adsorbent.

**Figure 4.** SEM micrographs of WTR (a) a-WTR (b) and h-WTR(c).
4. Conclusions
Results show that a low-cost carbonaceous adsorbent is feasibly produced from WTR. Adsorbents with high surface area and high pore volume were successfully obtained using heat treatment approach. 90% and 82% Cu(II) absorption were achieved using 0.5 g of 40 mesh size h-WTR and a/h-WTR respectively. On the other hand, h/a-WTR and a-WTR presented low capacity of Cu(II) adsorption.

Acknowledgments
The author gratefully thanks Department of Materials Science, Faculty of Science, Chulalongkorn University for facility support in this work. In addition, author expresses gratitude for financial scholarships from the center of excellence on petrochemical and materials technology.

References
[1] Inyang M I, Gao B, Yao Y, Xue Y, Zimmerman A, Mosa A, Pullammanappallil P, Ok Y S and Cao X 2016 *Crit Rev Env Sci Tec* **46** 406–433
[2] Mousavi H Z, Hosseinifar A and Jahed V 2010 *J. Serb. Chem. Soc.* **75** 6 845–853
[3] Carolin C F, Kumar P S, Saravanan A, Joshiba G J and Naushad M 2017 *J. Environ. Chem. Eng.* **5** 2782–99
[4] Silva J E, Paiva A P, Soares D, Labrincha A and Castro F 2005 *J. Hazard. Mater. B.* **120** 113–118
[5] Asheh S A and Banat F 2000 *Adsorpt. Sci. Technol.* **18** 685-700
[6] Wang Q, Gao W, Liu Y, Yuan J, Xu Z, Zeng Q, Li Y and Schröder M 2014 *Chem. Eng. J.* **250** 55–65
[7] Nuilerd T, Pongyeela P and Chungsiriporn J 2018 *Songklanakarin J. Sci. Technol.* **40** 264-270
[8] Zhao J J, Shen X J, Domene X, Alcañiz J M, Liao X and Palet C 2019 *Sci. Rep.* SR9(2019)9869
[9] Do Q C, Choi S, Kim H and Kang S 2019 *Appl. Sci.* AS9(2019)5375
[10] Mohajerani A et al. 2020 *Resour Conserv Recycl* RCR155(2020)104679
[11] Fazli A and Rodrigue D 2020 *J. Compos. Sci.* JCS4(2020)103
[12] Vizuete E M, Garcia A M, Gisbert A N, González C F and Serrano V G 2005 *J. Hazard. Mater.* **119** 231–238
[13] Gupta V K, Gupta B, Rastogi A, Agarwal S and Nayak A 2011 *Water Res.* **45** 4011-55.
[14] Hernandez E H, Gamez J F H, Cepeda L F, Munoz E J C, Corral F S, Rosales S G S, Velazquez G N, Morones P G and Martinez D I S 2017 *J. Appl. Polym. Sci.* JAPS(2017)44864
[15] Yang X, Wan Y, Zheng Y, He F, Yu Z, Huang J, Wang H, Ok Y S, Jiang Y and Gao B 2019 *Chem. Eng. J.* **366** 608–621
[16] Taleb D A, Hamid H A, Deris R R R, Zulkifli M, Khalil N A and Yahaya A N A 2020 *Mater Today Proc* **31** 178–186
[17] El-Moselhy K M, Azzem M A, Amer A and Al–Prol A E 2017 *Phys Chem Ind J.* PCIJ12(2017)2
[18] Jiang Z, Liu Y, Sun X, Tian F, Sun F, Liang C, You W, Han C and Li C 2003 *Langmuir* **19** 731-736