Removal of Cu(II) from wastewater by waste tire rubber ash

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Abstract: The influence of pH, adsorbent dose, initial Cu(II) concentration and contact time on the removal of Cu(II) from aqueous solution by the batch adsorption technique using waste tire rubber ash as a low-cost adsorbent was investigated. The adsorption equilibrium was achieved after 2 h at pH 4–6, the optimum for the adsorption of Cu(II) ions. A dose of 1.5 g/L of adsorbent was sufficient for the optimum removal of copper ions. The experimental data were analyzed by the Langmuir and Freundlich isotherms and the corresponding sorption constants were evaluated. The adsorption kinetics data were fitted by a first-order equation. The cost of removal is expected to be quite low, as the adsorbent is cheap and easily available in large quantities. The present study showed that waste tire rubber ash was capable of removing copper ions from industrial wastewater samples.

Keywords: removal; copper; waste tire rubber ash; wastewater; isotherm.

INTRODUCTION

Today contamination of water by toxic heavy metals resulting from the discharge of industrial wastewater is a worldwide environmental problem. Many industries, particularly in metal processing operations and refineries, represent significant sources of heavy metal emissions. Unlike organic compounds, soluble heavy metals, such as copper, cadmium, lead, and chromium, are non-biodegradable and toxic even at trace levels. Heavy metals can accumulate in living organism and cause various diseases.[1–4]

Copper and its compounds are widely used in many industries and there are many potential sources of copper pollution. The continued intake of copper by humans leads to necrotic changes in the liver and kidney, mucosal irritation; wide spread capillary damage, depression, gastrointestinal irritation, and lung cancer.[5] According to the Safe Drinking Water Act, the permissible limit of copper in

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drinking water is 1.3 mg/L.[6] Excessive copper concentrations can lead to weakness, lethargy and anorexia, as well as damage to the gastrointestinal tract.[7] Therefore, there is a considerable need to treat industrial effluents containing such heavy metals prior to discharge to protect public health. The metal needs to be removed from industrial effluents before discharge into the environment to mitigate any impact on plant, animal and human receptors.

The most common treatment processes for metal contaminated wastewater include: chemical precipitation, membrane filtration, reverse osmosis and ion exchange. These methods have been found to be limited, since they often involve high capital and operational costs and may also be associated with the generation of secondary wastes which present treatment problems.[8–12]

Adsorption is arguably the most important type of physicochemical processes responsible for the removal of heavy metals from aqueous environments. In recent years, adsorption was shown to be an economically feasible method for the removal of metal ions from water and wastewater. The biggest barrier in the industrial application of this process is the high cost of adsorbents presently available for commercial use. The cost of the application of adsorption technologies can be reduced if the adsorbent is inexpensive; hence, the search for low-cost adsorbents that have metal-binding capacities has intensified. This has led many workers to search for cheaper alternatives among plant wastes or industrial by--products, such as granular red mud,[13] chitosan,[14,15] potato peel,[16] fired coal fly ash,[17] sugar beet pulp,[18,19] palm kernel husk,[20] bagasse fly ash,[21] modified cellulosic materials,[22] spent grain,[23] peanut husks carbon,[24] sawdusts,[25] papaya wood,[26] sugarcane bagasse,[27] rice husk,[28] and pomegranate peel.[29]

Waste tires have been a major management and disposal problem in many countries for decades. Many waste tires are currently stockpiled in various countries around the globe. These stockpiles are dangerous because they pose a potential environmental concern, are fire hazards and provide breeding grounds for mosquitoes. The practice of disposing waste tires in landfills is becoming unacceptable because of the rapid depletion of available landfill sites.

This work is focused on the removal of Cu(II) ions from aqueous solutions using waste tire rubber ash (WTRA) as an adsorbent. The influences of pH, contact time, initial iron concentration, temperature and adsorbent dosage on the removal of Cu(II) from wastewater and water solutions were investigated. Equilibrium isotherm data were analyzed by the Langmuir and Freundlich equations using linear regression analysis. The adsorption efficiency towards copper ion removal was tested using different industrial wastewaters.

EXPERIMENTAL

Material

Analytical grade chemicals were used throughout the investigation. Merck salts and standards used for quantification were of high purity (99.9 % or more) having trace metal

contents far below their detection limits. Aqueous standard solutions of Cu(II) were prepared by dissolving an accurately weighed amount of $Cu(NO_3)_2$ salt in deionized water so as to yield a metal ion concentration of 1000 mg L^{-1}. Appropriate aliquots were taken from these standards for subsequent dilution to the desired concentration level. NaOH and HCl solutions, both 0.10 mol L^{-1}, were used for pH adjustment. A Metrohm (model E-632) pH meter was used for the pH measurements. Polyethylene bottles were selected as containers. The bottles were first cleaned with a metal-free non-ionic detergent and washed with tap water. They were then soaked in 1:1 HNO_3 + H_2O solution for 24 h at 70 °C and subsequently rinsed thrice with de-ionized water. The total copper concentrations in the solution samples were determined using flame atomic absorption spectroscopy (FAAS) equipped with copper hallow cathode lamp (λ = 324.8 nm) and acetylene–air as the fuel-oxidant.

Adsorbent preparation and characterization

The material used in this study was obtained by treatment of waste tire rubber in order to prepare the desired ash. Thus, it was first washed with detergent solution and then with dilute HCl in order to remove soil debris. Then the clean and dry parts were burnt and the residue was taken in a porcelain crucible and burnt completely at 500 °C in a muffle furnace for 4 h. The cooled ash was then washed with a very dilute acidic solution, such as 0.0010 mol L^{-1} HCl to remove salts of metals, such as Na, K and Ca. Subsequently, the mixture was filtered out using a Whatman grade 42 filter paper. Then the adsorbent was washed with 100 mL of double distilled water and dried at 105 °C for 2 h before use.

The adsorbent was characterized by standard methods. The microstructure and surface morphology of the adsorbent samples were characterized by SEM images of WTRA particles obtained using a Phillips PW3710 Field Emission Scanning Electron Microscope (SEM) with an accelerating voltage of 15.0 kV.

Adsorption studies

Adsorption isotherms were determined using the batch equilibrium method. The adsorption of Cu(II) was studied after adding 50 mg of WTRA into an aqueous solution containing the desired Cu(II) concentration (50–500 mg L^{-1}), adjusting the pH of the solution to between 2 and 6, shaking at 150 rpm for 2 h at 25 °C in a reciprocating shaker and then the samples were centrifuged at 5000 rpm for 5 min. The WTRA particles were separated from the suspensions by filtration through a 0.45 µm membrane filter. The residual concentration of copper ions was determined by atomic absorption spectrometry.

In addition to the adsorption tests, a set of blank tests with WTRA was conducted in order to evaluate the removal by metal hydroxide precipitation at various pH values. The amount of Cu(II) adsorbed on the WTRA was calculated from the difference between the initial concentration and the equilibrium concentration of Cu(II). The percent Cu(II) removal, R_e, was calculated using the following equation:

$$R_e = 100\frac{c_i - c_f}{c_i} \tag{1}$$

where c_i and c_f are the initial and equilibrium concentrations of the adsorbate, respectively. The reported value of Cu(II) ions adsorbed by WTRA in each test was the average of at least three measurements.

RESULTS AND DISCUSSION

Adsorbent characteristics

The characteristics of the WTRA were as follows: surface area (BET), 410 m^2/kg, specific gravity, 2.35, average particle size, 9.0 μm, chemical composition: SiO_2 (26.5 %), Al_2O_3 (8.7 %), TiO_2 (1.0 %), Fe_2O_3 (9.3 %), MgO (6.4 %), CaO (12.9 %), Na_2O (1.4 %), K_2O (1.1 %), SO_3 (1.6 %) and Zn (20.2 %).

The SEM images of the WTRA particles are shown in Fig. 1.
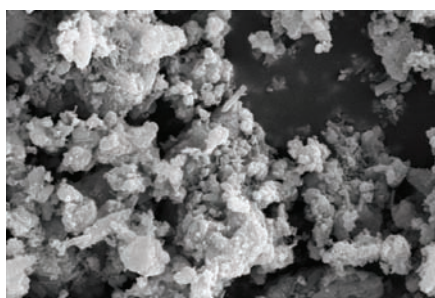

Fig. 1. SEM Images of the WTRA particles.

Adsorption studies

Effect of contact time. The results of the effect of equilibrium time on the sorption of Cu(II) by WTRA are shown in Fig. 2, which clearly shows that the adsorption of Cu(II) ions onto the WTRA was relatively fast and the complete adsorption equilibrium between the two phases was obtained after 2 h. The results show that 120 min was a sufficient time for copper adsorption onto the WTRA. The fast metal uptake by the sorbents may be attributed to their highly porous and mesh structure, which provides ready access and a large surface area for the sorption of the metal ions onto the binding sites. Thus, for subsequent experiments, an equilibration time of 2 h was chosen for the sake of convenience (Fig. 2).
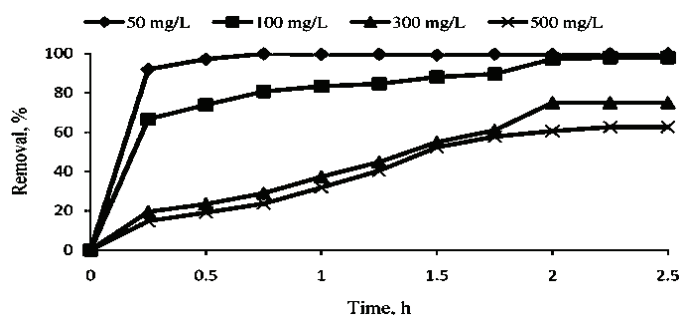

Fig. 2. Effect of contact time on the sorption of copper by WTRA. Conditions: 1.5 g L^{-1} of WTRA, 100 mL of Cu(II) solution, temperature: 25 °C.

Effect of adsorbent dose. The removal of metal ions is a function of adsorbent dosage; hence, the efficiency of the WTRA was evaluated at different doses using the percent removal of copper. The experiments were conducted at a constant initial Cu(II) concentration (100 mg L^{-1}), contact time (2 h), temperature (25±1 °C), stirring speed (150 rpm) with varying adsorbent doses (0.1–2.5 g L^{-1}). The measurement of the percentage Cu(II) removal as a function of time at different doses indicated that the removal of Cu(II) increased with increasing adsorbent dose (Fig. 3). The increase in copper removal with adsorbent dose can be attributed to the increased surface area and the availability of more adsorption sites. The removal efficiency was found to increase proportionally with the amount of WTRA until a certain value was reached; afterwards, the removal efficiency remained constant even if WTRA was added. Therefore, 1.5 g L^{-1} of adsorbent was sufficient for the quantitative removal of copper from wastewater (Fig. 3).
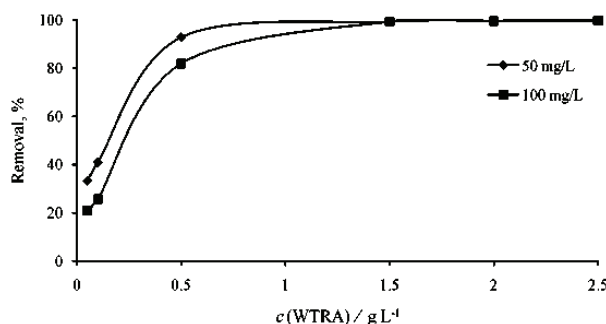

Fig. 3. Effect of WTRA dosage on the removal of Cu(II). Conditions: 100 mL of Cu(II) solution, contact time: 2 h, temperature: 25 °C.

Effect of pH. WTRA is a strong alkali material, which exhibits a pH of 10–13 when added to water, and its surface is negatively charged at high pH values. Hence, it can be expected that metal ions can be removed from aqueous solutions by precipitation or electrostatic adsorption. In fact, a number of studies were conducted to show the effectiveness of fly ash in the removal of heavy metal ions from aqueous solutions.[30]

All experiments were performed in the pH range of 2.0–6.0, at which values chemical precipitation is avoided. Thus the metal removal could be related to the adsorption process. Adsorption of Cu(II) onto the WTRA (1.5 g L^{-1}) was studied at various pH values to optimize the removal of Cu(II) at 25 °C. It is apparent that the uptake was low at lower pH values; however, with increasing pH, a significant enhancement in the adsorption was recorded. The optimum pH for the removal of Cu(II) was found to be in the range 4.5–6.0, with a removal of about 99.8 % Cu(II) from the solution.

The low adsorption capacity at pH values below 4.5 was attributed to hydrogen ions that compete with the metal ions for the sorption sites.[31] In other words, at lower pH values, due to protonation of the binding sites resulting from the high concentration of protons, the negative charge intensity on the sites was reduced, resulting in a reduction or inhibition of the binding of metal ions. At pH value higher than 6, the copper ions precipitated as its hydroxide, which decreased the rate of adsorption and subsequently the percent removal of metal ions.

Effect of temperature. The adsorption mechanism (chemical or physical) is often an important indicator to describe the type and level of interactions between the adsorbate and adsorbent. If the adsorption decreases with increasing temperature, it may be indicative of physical adsorption and the reverse is generally true for chemisorption. However, there are a number of contradictory cases in the literature.[32]

The effect of temperature on the removal of copper by the WTRA was studied at 1, 25 and 52 °C for concentration range 50–200 mg L^{-1} at pH 6.0. The results showed that the adsorption increased with increasing temperature, which means that the removal of Cu(II) was favored at high temperatures. Thus, the removal process was endothermic (Fig. 4).
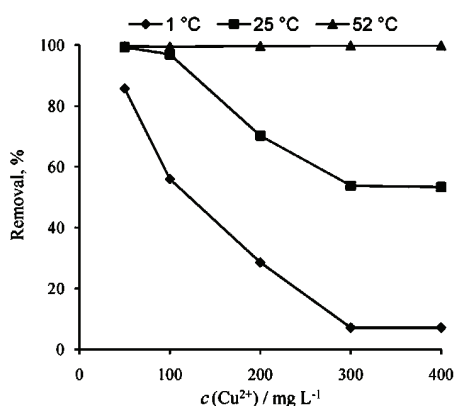

Fig. 4. Effect of temperature on the removal of Cu(II). Conditions: 1.5 g L^{-1} of WTRA, 100 mL of Cu(II) solution, contact time: 2 h; ♦ – 1, ■ – 25 and ▲ – 52 °C.

Adsorption isotherm. Adsorption isotherms play a crucial role in the predicttive modeling procedures for the analysis and design of adsorption system. Therefore, in this study, the adsorption data of Cu(II) were tested with the Langmuir and Freundlich isotherm models. The equilibrium studies were performed at 25 °C for the contact time required to reach adsorption equilibrium. A Langmuir isotherm can be represented by the following equation:

$$\frac{c_e}{Q_e} = \frac{1}{Q_{max}b} + \frac{c_e}{Q_{max}} \tag{2}$$

where c_e is the equilibrium concentration, Q_e is the amount of copper adsorbed, and Q_{max} and b are Langmuir constants related to the adsorption capacity and energy, respectively.

The data from this study showed that a straight line was obtained when c_e/Q_e was plotted against c_e. This indicates that the Langmuir isotherm was followed under the present conditions with $R^2 = 0.997$.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as:

$$Q_e = K_F c_e^{1/n} \tag{3}$$

The linear form of this equation can be written as:

$$\ln Q_e = \ln K_F + (1/n)\ln c_e \tag{4}$$

where K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The intercept and the slope of the linear plot of $\ln Q_e$ *vs.* $\ln c_e$ for given experimental conditions provide the values of K_F and $1/n$, respectively.

In general, the Langmuir model fitted the experimental results slightly better than the Freundlich model. This suggests that the adsorption of Cu(II) ions by WTRA is a monolayer-type and agrees with the observation that the metal ion adsorption from an aqueous solution usually forms a layer on the adsorbent surface (Table I).

TABLE I. Langmuir and Freundlich isotherm constants

Ion	Freundlich isotherm			Langmuir isotherm		
	K_F	n	R^2	Q_{max} / mg g^{-1}	b / mg^{-1} L^{-2}	R^2
Cu(II)	1.42	0.66	0.96	34.3	0.064	0.99

Kinetic modeling

In order to investigate the controlling mechanism of the sorption process, such as mass transfer and chemical reaction, the Lagergren kinetics first-order model was used to test the experimental data of copper sorption by WTRA.

The Lagergren kinetics equations have been most widely used for the adsorption of an adsorbate from an aqueous solution, which is expressed by Eq. (5):

$$\log (q_e - q_t) = \log q_e - k_t/2.303 \tag{5}$$

where q_e and q_t are the amounts of Cu(II) adsorbed at equilibrium and at time t, in, and k_t is the first order rate constant. This equation was applied to the present studies of Cu(II) adsorption. The plots were found to be linear, indicating that the Lagergren Equation is applicable to Cu(II) adsorption on WTRA and the adsorption was first order and the value of first-order rate constant k_t was evaluated to be 0.0012 min^{-1}.

Treatment of metal industry wastewater

Based on the promising results obtained for copper ions removal from aqueous solutions, tests were conducted to evaluate these results using real wastewater. The wastewater used was taken from a local metal plating factory. It had a pH of 4.25 and contained Cu(II) at a concentration of 1.89 mg L^{-1}. Tests were conducted over a range of pH values (2–6) with varying WTRA concentrations. The samples were shaken at 25 °C for 2 h. At the end of this period, the solutions were separated by filtration and the residual metal concentration in the supernatant was determined by atomic absorption spectrophotometry. As observed in the tests with artificial solutions of Cu(II), the removal increased with increasing WTRA concentration, as well as increasing pH value. When the WTRA dosage was increased to 1.5 g L^{-1}, the Cu(II) removal increased to 100 %. Therefore, waste tire rubber ash was effective in removing Cu(II) from wastewater.

CONCLUSIONS

The results obtained in this study demonstrate that waste tire rubber ash can be used as an excellent adsorbent to remove copper from wastewaters with a good efficiency and low cost. Several parameters were studied and maximum adsorption was found to occur in the pH range 4.5–6.0 within 120 min-contact. The adsorption efficiencies increased with increasing contact time and initial metal concentration; the maximum observed capacity of the material was 34.3 mg/g of material. Furthermore, it can be concluded that waste tire rubber ash holds great potential to be an effective adsorbent for the removal of Cu(II) from wastewater samples.

И З В О Д

УКЛАЊАЊЕ Cu(II) ИЗ ОТПАДНИХ ВОДА КОРИШЋЕЊЕМ ПЕПЕЛА ДОБИЈЕНОГ САГОРЕВАЊЕМ ОТПАДНИХ АУТОМОБИЛСКИХ ГУМА

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Испитан је утицај pH, дозе адсорбента, почетне концентрације Cu(II) и времена контакта на уклањање Cu(II) из воденог раствора техником шаржне адсорпције, коришћењем отпадног пепела од сагоревања аутомобилских гума као јефтиног адсорбента. Адсорпциона равнотежа је постизана након 2 часа при pH 4 до 6, што је оптимум за адсорпцију Cu(II) јона. Доза од 1,5 g/L адсорбента је била довољна за оптимално уклањање бакарних јона. Експериментални резултати су анализирани Лангмировом и Фројндлиховом изотермом, и одређене су одговарајуће константе сорпције. Подаци о кинетици адсорпције апроксимирани су једначином првог реда. Очекује се да трошак уклањања буде низак, с обзиром да је адсорбент јефтин и доступан у великим количинама. Ова студија је показала да пепео добијен са-

горевањем аутомобилских гума може да уклони јоне бакра из узорака индустријске отпадне воде.

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REFERENCES

1. L. R. B. Sanchez, B. S. V. de la Riva, J. M. C. Fernandez, R. Pereiro, A. S. Medel, *Talanta* **55** (2001) 1071
2. F. Liu, X. Luo, X. Lin, L. Liang, Y. Chen, *J. Hazard. Mater.* **171** (2009) 802
3. V. K. Gupta, C. K. Jain, I. Ali, M. Sharma, V. K. Saini, *Water Res.* **37** (2003) 4038
4. F. Gode, E. Pehlivan, *J. Hazard. Mater.* **100** (2003) 231
5. S. Rengaraj, J. W. Yeon, Y. Kim, Y. Jung, Y. K. Ha, W. H. Kim, *J. Hazard. Mater.* **143** (2007) 469
6. P. D. Johnson, M. A. Watson, J. Brown, I. A. Jefcoat, *Waste Manag.* **22** (2002) 471
7. T. Theophanides, J. Anastassopoulou, *Oncology/Haematology* **42** (2002) 57
8. J. Zeng, H. Ye, Z. Hu, *J. Hazard. Mater.* **161** (2009)1491
9. E. Pehlivan, T. Altun, *J. Hazard. Mater.* **134** (2006) 149
10. S. Rengaraj, J. W. Yeon, Y. Kim, Y. Jung, Y. K. Ha, W. H. Kim, *J. Hazard. Mater.* **143** (2007) 469
11. A. Baraka, P. J. Hall, M. J. Heslop, *J. Hazard. Mater.* **140** (2007) 86
12. J. W. Patterson, *Industrial wastewater treatment technology*, Butterworth-Heinemann, Stoneham, MA, 1985, p. 175
13. C. Zhu, Z. Luan, Y. Wang, X. Shan, *Sep. Purif. Technol.* **57** (2007) 161
14. A. T. Paulino, L. B. Santos, J. Nozaki, *React. Funct. Polym.* **68** (2008) 634
15. M. Radetić, D. Radojević, V. Ilić, D Jocić, D. Povrenović, B. Potkonjak, N. Puac, P. Jovančić, *J. Serb. Chem. Soc.* **72** (2007) 605
16. T. Aman, A. A. Kazi, M. U. Sabri, Q. Bano, *Colloids Surf. B* **63** (2008) 116
17. A. Papandreou, C. J. Stournaras, D. Panias, *J. Hazard. Mater.* **148** (2007) 538
18. E. Pehlivan, B. H. Yanık, G. Ahmetli, M. Pehlivan, *Bioresour. Technol.* **99** (2007) 3520
19. H. S. Altundogan, *Process Biochem.* **40** (2005)1443
20. J. A. Omgbu, V. I. Iweanya, *J. Chem. Ed.* **67** (1990) 800
21. V. K. Gupta, I. Ali, *J. Colloid Interface Sci.* **271** (2004) 321
22. F. E. Okieimen, D. E. Ogbeifun, G. N. Nwala, G. A. Kumsah, *Bull. Environ. Contam. Toxicol.* **34** (1985) 866
23. K. S. Low, C. K. Lee, S. C. Liew, *Process Biochem.* **36** (2000) 59
24. S. Ricordel, S. Taha, I. Cisse, G. Dorange, *Sep. Purif. Technol.* **24** (2001) 389
25. B. Yu, Y. Zhang, A. Shukla, S. S. Shukla, K. L. Dorris, *J. Hazard. Mater.* **80** (2000) 33
26. A. Saeed, M. W. Akhter, M. Iqbal, *Sep. Purif. Technol.* **45** (2005) 25
27. S. C. Ibrahim, M. A. K. M. Hanafiah, M. Z. A. Yahya, *J. Agric. Environ. Sci.* **1** (2006) 179
28. S. Mohan, G. Sreelakshmi, *J. Hazard. Mater.* **153** (2008) 75
29. E.-S. Z. El-Ashtoukhy, N. K. Amin, O. Abdelwahab, *Desalination* **223** (2008) 162
30. H. Cho, D. Oh, K. Kim, *J Hazard Mater.* **127** (2005) 187
31. C. P. Huang, C. P. Huang, A. L. Morehart, *Water Res.* **25** (1991) 1365
32. M. S. Celik, R. H. Yoon, *Langmuir* **7** (1991) 79.