

284. Purification of Copper Ion Contaminated Industrial Water by Activated Carbon Prepared from Scrap Rubber Tyres

Muhammad Ashfaq Sajjid^a, Sylvia Benjamin^{b,*}

^a Obeikan Investment Group

^b Forman Christian College - A Chartered University, Lahore

*Email address: s_e_benjamin@yahoo.com

Abstract

Water purification is essential for environmental sustainability of human life and life in water bodies. Commercially available activated carbon is costly and imported in Pakistan. Activated carbon was prepared from cost effective and non-degradable scrap rubber tyres by simple method. Carbon obtained after the dry distillation of scrap tyres was treated with 5% solution of Barium chloride and 0.4 N solution of hydrochloric acid and verified using ethylene blue solution and FTIR. The removal of copper ions from aqueous solutions by the prepared tyre activated carbon was investigated in the present studies. The copper ion removal tests by the prepared tyre activated carbon were carried out as the function of pH, adsorbent concentration, contact/stirring time of the adsorbent with the adsorbate and the concentration of adsorbate. All these factors have a detrimental effect on copper ion removal by the prepared tyre activated carbon.

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Keywords: Activated carbon; adsorbent; copper ions; contact time; pH; scrap tyres.

1. Introduction

Industrialization and urbanization has added positively to the world in limitless ways. However, anthropogenic activities have degraded the environment drastically. Uncontrolled industrial emissions have loaded the ecosphere. Many of the earth's ecosystems are pushed to the critical edge of depletion or irreversible change. Wasteful and irresponsible use of natural resources has created an alarming state of affairs, which needs to be rectified imperatively without further leniency to the perpetrators. Many countries in the world today are struggling with drinking water scarcity due to throw of toxic wastes in water bodies. The aquatic life is threatened and many species are simply eradicated. 50 million people do not have access to safe drinking water [1]; and roughly expanding to a fig of 1 billion, suffering from disease, education and economic divest is noticeable.

Heavy metal presence in water is of serious concern due to their toxic effects on plants and aquatic organisms [2]. The scenario can be graver due to the bioavailability, accumulation and effects of heavy metals in sediments [3-4], and leaching and seepage into ground water [5]. Incorporation in the food chain is disturbing and an indicator of environmental degradation posing serious threat to aquatic and human health [6-7].

People living in industrial vicinity are more at risk of water borne diseases. Copper ion enters water bodies through various sources as metallurgical industries, printing industries, copper pipes and taps and copper mining activities etc. Copper ion effects on water species have been elaborated in the report by EPA [8]. Dietary copper in the range of 1-3 mg/day [9] is required by the human body. Ingestion of higher copper (II) ions can cause lethal effects as gastrointestinal bleeding, intravascular haemolysis, abnormal methoglobin, liver cell damage, acute renal failure and oliguria [10]. Lower doses cause typical symptoms of food poisoning [11].

Drinking water shortage is surmounting in many parts of the world due to uncontrolled release of pollutants in water bodies. Expansion of rural areas has started to touch the chemical and other industries that were once constructed in the outskirts of cities. The problem is acute in third world countries where people are unable to

afford bottled water. Water filtration plants are scarce and over used and under maintained. The infant death toll is rising due to water borne diseases and the situation is worsening every day.

Removal of heavy metals at high concentration from polluted water can be readily accomplished by flotation, chemical precipitation, electrolytic removal, separation by membrane and chelation. However, these methods are costly and mostly irreversible. In water bodies, water chemistry plays an important role in reducing the pollutant ion concentration. Copper ion concentration also varies in water sphere affected by several parameters [12]. The present studies focus upon the use of activated carbon, prepared from rubber tyre waste. The prepared activated carbon is used as an adsorbent for the removal of copper (II) ions from aqueous solution. The important effect of pH, contact time, temperature and concentration of the adsorbate are studied. The aim was to investigate a cost effective source of activated carbon i.e., utilization of non-degradable scrap rubber tyres and rationalize optimum conditions required for copper ions removal from water.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of Activated Carbon from Scrap Rubber Tyres.

Old and used rubber tyres were collected from the local market. The tyre scrap was cut into small pieces and crushed, grinded into small sized particles. The small sized tyre pieces were washed several times, with distilled water to remove impurities. These were then air dried thoroughly.

600 gms of the dried scrap tyre pieces were processed into dry distillation at 360 °C in a round bottomed flask fitted with a water condenser inside fume cupboard. The apparatus is described in detail elsewhere [13]. During the dry distillation the obnoxious gases released into the atmosphere and the oil got extracted into conical flask as distillate. Thereby chars and oils were separated. The char residue obtained was heated in the muffle furnace at 800-900 °C for 30 minutes. The char sample i.e., carbon was cooled down at room temperature.

2.2. Confirmatory tests for Tyre activated carbon.

The air cooled carbon sample was soaked in 5% BaCl₂ solution for 12 hrs. The filtered sample was analysed by Fourier transform infra-red (FTIR) spectroscopy. The spectra of tyre activated carbon were recorded on a Varian 640 FTIR spectrophotometer in the range 400- 4000 cm⁻¹, using KBr dilution and finely powdered KBr as reference. The activated carbon was washed with 0.4N HCl and finally with distilled water in order to remove the oxides and soluble impurities. The final sample was dried in an oven overnight at 105 °C. The dried tyre activated carbon was sieved. 200 mesh size of the tyre activated carbon was selected for further studies.

The tyre activated carbon adsorption capacity was confirmed through the Methylene Blue test. 0.2gm tyre activated carbon was immersed in 10ml of 1% methylene blue solution in a 50ml beaker. Same test was performed with commercially available activated carbon. The adsorption efficiency of tyre activated carbon was measured against commercially available Merck activated carbon at λ_{max} of 660nm.

Analytical grade copper sulphate salt (CuSO₄.5H₂O) was used for the preparation of stock solution. The copper salt was dried in an oven for overnight at 50 °C and cooled in desiccators. 1000 ppm stock solution (1L) of copper ion made with double de-ionised water was used in this study. Other solutions i.e., 10 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm copper ion concentrations were prepared by the dilution of the stock solution with double de-ionised water.

2.3. Tests on performance of Tyre Activated carbon

2.3.1 The effect of tyre activated carbon amount on removal of copper ion.

0.1gm, 0.2gm, 0.3gm, 0.4gm and 0.5gm of tyre activated carbon were added to 25 ml of 200 ppm solution of Copper ion in 50 ml volumetric flasks and stirred for 3 hrs on magnetic stirrer at 200 rpm. The solutions were filtered and the adsorption of copper ions by the tyre activated carbon for all the sample concentrations were determined on Varian atomic absorption spectrophotometer. An acetylene-air flame and lamp current 7 mA was used for the copper ion determination.

2.3.2. The effect of copper ion concentration on the adsorption efficiency of tyre activated carbon.

0.2 gm of tyre activated carbon was added to 25 ml of 10 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm Cu^{2+} ion solutions in 50 ml volumetric flasks. The solutions were stirred for 3 hrs on magnetic stirrer at 200 rpm and then filtered. Adsorption of copper ions by the tyre activated carbon for all the sample concentrations were determined by atomic absorption.

2.3.3. The effect of solution pH on the adsorption capacity of tyre activated carbon.

0.2 gm of tyre activated carbon was added to 200 ppm solution of Copper ions in 50 ml volumetric flask (x3) with pH maintained at 4, 7 and 10, monitored by pH electrode attached to pH meter. The three solutions were stirred for 3 hrs on magnetic stirrer at 200 rpm. After filtration, the copper ion concentration remaining in the solution was determined.

2.3.4. The effect of stirring contact time on adsorption capacity of tyre activated carbon.

0.2 gm of tyre activated carbon was added to 200 ppm solution of Copper ions in 50 ml volumetric flask (x3). The solutions were stirred for different time intervals i.e., 1, 2 and 3 hrs on magnetic stirrer at 200 rpm and the copper ion concentration remaining in the solution was determined.

3. Results and Discussions

Water pollution and drinking water shortage crises have led scientists worldwide to explore low cost adsorbents [13-14]. Activated carbon is a very useful material for removal of pollutant ions especially from water. Such carbons have been prepared earlier from waste tyres but the methods are laborious and more expensive [15-16]. The waste tyre activated carbon obtained in the present investigation was prepared by the dry distillation process of waste rubber tyres followed by heating in muffle furnace at 800-900 °C for 30 minutes. It was identified by FTIR spectroscopy. The spectra mainly showed two weak peaks. The first peak appeared at 1578-1667 cm^{-1} due to C=C stretching vibration. The second peak was observed at 2364 cm^{-1} due to symmetric or asymmetric stretching of aliphatic band in -CH, -CH₂ or -CH₃. The first peak is also reported by A. Belgacem et. al [17], besides -OH and -PH bonding. They did cryogenic and ambient grinding of the tyres and treated it with phosphoric acid before carbonization at 650 °C in inert atmosphere of nitrogen for 2 hrs and 30 minutes.

The Tyre activated carbon immersed in methylene blue (1%) showed absorbance of 0.053 measured at 660 λ_{max} . The Merck activated carbon sample showed an absorbance of 0.035 at same test conditions. This confirmed that the prepared tyre activated carbon had proper absorption properties for the dye at room temperature.

The effect of copper ion concentration on the adsorption efficiency of tyre activated carbon was studied by adding 0.2 gm (200 mesh size) of tyre activated carbon in 25 ml of 10 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm copper (II) solutions with a stirring time of 3 hrs on magnetic stirrer at 200 rpm. After filtration of solutions, adsorption of copper ions by the tyre activated carbon was measured by atomic absorption spectrophotometer. The results are presented in Fig. 1.

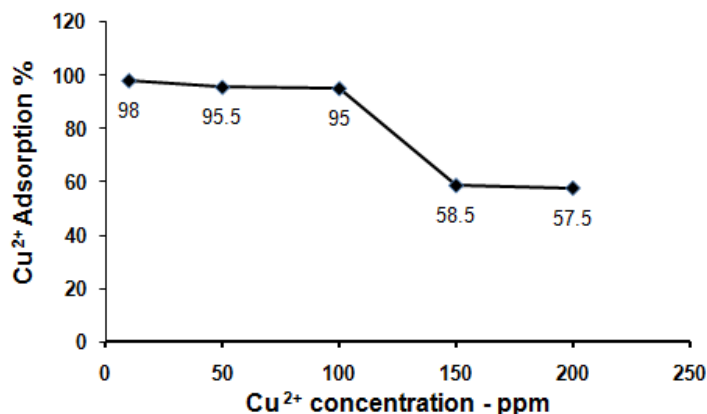


Fig. 1. Effect of Cu (II) ion concentration on adsorption by the tyre activated carbon

The removal of metal ions from aqueous solution by adsorption is highly dependent on the concentration of the Cu²⁺ ion solution that affects the adsorption efficiency of tyre activated carbon. This important parameter is studied earlier by several scientists [18-19]. The adsorption is applicable for a specific range of concentration and after this specific range further adsorption declines due to the blockage of all the active site on the tyre activated carbon. Fig. 1 shows that the adsorption decreased when the concentration of the adsorbate ions increased. Here the amount of adsorbent has become the limiting factor. The maximum adsorption is observed for low concentration of Cu(II) ions i.e., 10 ppm. For 0.2 gm of tyre activated carbon, 98% removal of Cu²⁺ ions from a 10 ppm copper solution is possible.

The effect of tyre activated carbon amount on the removal of copper ion was investigated with 200 ppm Cu(II) solution that showed limited adsorption with 0.2gm of the adsorbent. 0.1 gm, 0.2 gm, 0.3 gm, 0.4 gm and 0.5 gm of tyre activated carbon were added to 25ml (200ppm Cu²⁺ solution) and stirred for 3 hrs at 200 rpm on magnetic stirrer. The solutions were filtered and the adsorption of copper ions by the tyre activated carbon was determined by atomic absorption spectrophotometer. The results are given in Fig. 2.

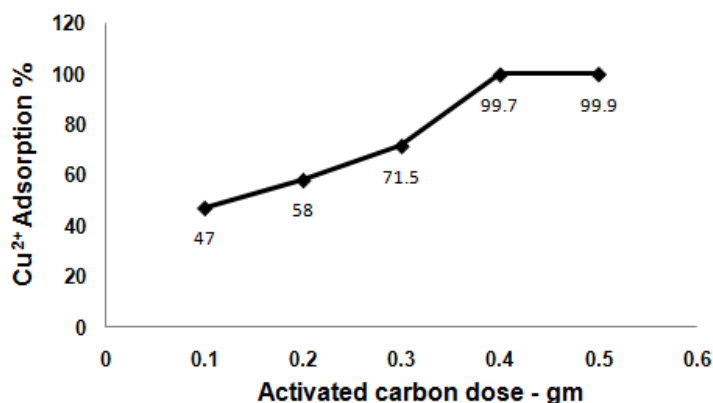


Fig. 2. Effect of tyre activated carbon dose on Cu (II) ion adsorption by the adsorbent

It can be seen that as the adsorbent amount is increased the removal of Cu²⁺ ions from the solution is facilitated as more sites are available for weak bonding of the solute ions. 100% adsorption of all the copper ions (200ppm) can be effectively achieved with 0.4 gm of the tyre activated carbon. These results support the data shown in fig. 1.

The effect of solution pH on the adsorption capacity of tyre activated carbon was studied by immersing 0.2 gm of tyre activated carbon into 25 ml of Cu^{2+} ions (200ppm) solution for a contact time of 3 hours with stirring at 200 rpm on a magnetic stirrer. The pH of the Cu^{2+} ion solutions was maintained at 4, 7 and 10. The solutions were filtered and the copper ion concentration was checked by Atomic absorption spectrophotometry. The effect of pH on the adsorption of Cu^{2+} ions is presented in Fig.3.

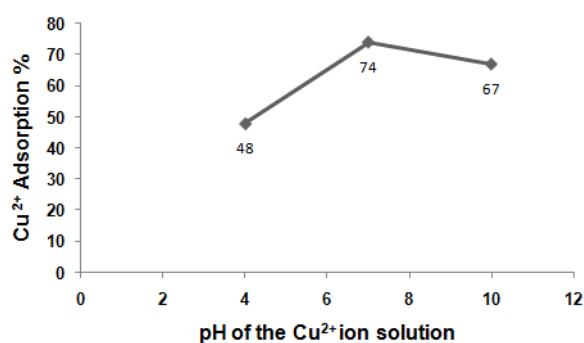


Fig. 3. Effect of pH on the adsorption of Cu^{2+} ions by the tyre activated carbon

Several scientists²⁰⁻²³ have studied the effect of solution pH on the adsorption of metal ions by various sources. Fig. 3 shows that the adsorption of Cu^{2+} ions is pH dependent phenomenon in the order neutral > basic > acidic. At low pH, presence of excess of H^+ ions promotes the dissolution of Cu^{2+} ions keeping them in solution. Besides, formation of H_3O^+ ions hinders the adsorption of Cu^{2+} ions. H_3O^+ ions compete with the Cu^{2+} ions for the active sites and preferably get attached to the charged surface of the tyre activated carbon. At a high pH-10, excess of OH^- ions disturbs the equilibrium. The system adjusts by the precipitation of Cu^{2+} ions forming $\text{Cu}(\text{OH})_2$ and releasing H^+ ion. Thus, the adsorption process is affected. Also, any excess, OH^- ions are preferably adsorbed at the active sites of the adsorbent. At neutral buffered pH-7, maximum adsorption of Cu^{2+} ions occurs i.e., 72 %. This adsorption amount is higher as compared to the Cu^{2+} ions solutions made with double deionised water that had slightly acidic pH 6.5. (Fig. 1 and Fig. 2). Dastgheib and Rockstraw²⁴ proposed a correlation for various parameters i.e., temperature, pH, carbon type and dosage. They have reported that a proton is released when a metal ion is adsorbed. This ratio is close to one, particularly at low concentrations. Mainly we have observed electrostatic interaction between the tyre activated carbon and Cu^{2+} ions. D. Božić et. al¹⁹ and V. Stanovick et al.²⁵, also observed the same trend i.e., least absorbance of Cu^{2+} ions at low pH with different adsorbents in separate studies, due to preferable attraction of H^+ ions towards the active sites on the adsorbent.

The effect of stirring contact time on adsorption capacity of tyre activated carbon was investigated by immersing 0.2 gm of tyre activated carbon in 200 ppm Cu^{2+} ion solution. The adsorbent was kept in contact with the adsorbate for different time intervals of 1, 2 and 3 hours on magnetic stirrer at 200 rpm. The solutions were filtered and the Cu^{2+} ions adsorbed were determined by atomic absorption technique. The results are presented in Fig. 4.

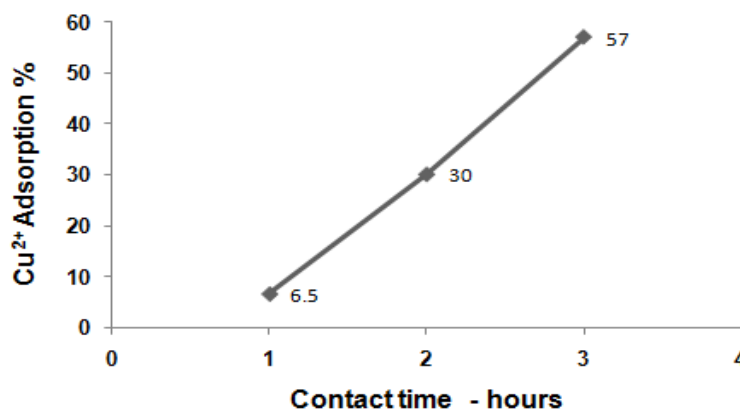


Fig. 4. Effect of contact time of tyre activated carbon on the adsorption of Cu²⁺ ions

The contact time of the adsorbent with metal ion solution is also an important factor which affects the adsorption efficiency of the adsorbent. The adsorption of Cu²⁺ ions is directly related to the contact/stirring time i.e., the adsorption of the metal ions also increase with the increase of the contact time for 200 ppm Cu²⁺ ion concentration. The linear correlation illustrated in Fig. 4 shows that constant stirring exposed active sites and adsorption process was facilitated. The transport of Cu²⁺ to the active sites of the tyre activated carbon would have been limited without stirring for being under diffusion control that would require longer hours for completion of adsorption onto the adsorbent.

4. Conclusions

Scrap rubber tyres were converted into a valuable carbonaceous adsorbent material. The scrap tyre activated carbon can adsorb 98 % of Cu²⁺ ions when present in weak concentration. The adsorption efficiency decreases after a certain Cu²⁺ ions concentration indicating expiry of the all the active sites on the adsorbate. The adsorption process improves with more adsorbent dosages as more active sites become available for physical adsorption of the polluting Cu²⁺ ions. Adsorption of copper by activated carbon derived from scrap rubber tyres was shown to depend significantly upon the pH of solution i.e., maximum adsorption of Cu²⁺ ions is achieved at pH-7 in comparison to pH 4 and pH-10 due to the competition of the Cu²⁺ ions with the OH⁻ and H⁺ ions. The contact time/stirring time of solution increases the Cu²⁺ ions removal by the scrap tyre activated carbon from solution, as buildup of Cu²⁺ ions for any site is prohibited and all unoccupied active sites become easily approachable.

The data obtained guides to convert non-degradable waste rubber tyres into a low cost valuable product for the purification of water that can be reused innumerable times before dispensed as compared to ordinary water filters. It can thus be a low cost, sustainable solution to clean industrial water for the local inhabitants and also preserve the aquatic environment.

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