



A STUDY OF THE DYNAMICS OF COPPER(II) IONS UPTAKE FROM AQUEOUS SOLUTIONS BY HUMAN HAIR USING CONDUCTIVITY AND pH MEASUREMENTS

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As the search for renewable resources for removal of pollutants from the environment grows, the use of biological sorbents has received a great deal of attention. Biological sorbents such as human hair have been explored due to their ready availability, renewability and effectiveness. This manuscript reports a study of the dynamics of copper(II) ions uptake by human hair using conductivity and pH measurements. The adsorption of these ions demonstrated a logarithmic behaviour, resembling first order kinetics, although the analysis showed a deviation from the first order kinetics. The maximum uptake of 288 $\mu\text{g g}^{-1}$ was reached after about 120 minutes of static equilibration using a solution of 100 ppm. Interestingly the adsorption seems to be intermediate between a simple chemisorption and ion exchange as evidenced by a deviation from the linearity when conductivity was plotted against the pH measurements. However there was a significant correlation ($R^2 = 0.9926$) between conductivity and pH in the case of a classical ion exchange resin – Amberlite CG 50.

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husks,¹³ pine cones,¹⁴ corn cobs,¹⁵ just to mention a few. Most of the generated biological waste reportedly has some degree of ability to bind most metal ions.¹⁶ The uptake in most of these sorbents is mainly due to the sugar-based polymers such as cellulose that form oxygen-rich moieties that chelate these metal ions.

Introduction

Heavy metals are metallic elements that have a relatively high density and toxic or poisonous at low concentrations.¹ They are metals of relative densities of 5 g mL^{-1} . Despite this, some of the heavy metals are vital for cell metabolism on living systems. However, the threat is posed when they accumulate high concentrations in the environment. Accumulation occurs when organisms take-up ions of heavy metals and store them in a rate which is faster than they are oxidised and/or reduced so that they be excreted.² The natural biogeochemical cycles are disrupted by various human activities causing increased deposition of heavy pollutants which without proper treatment poses significant threat to both environment and public health as they are non-biodegradable and therefore are persistent.³

In recent years, the need for safe and economic methods for elimination of heavy metals from wastewater has necessitated the research for low cost available methods and materials.⁴ The inorganic adsorbing materials that have been found effective for removal of heavy metals from aqueous samples include fly ash,⁵ zeolites,⁶ natural clays such as montmorillonite,⁷ just to name a few. Biological materials have recently received a great deal of attention not only due to their renewability but also because they are highly efficient with some taking up heavy metals up to 50 % of the biomass dry weight.⁸ The ability of living organisms to take in and accumulate heavy metals has been employed in phytoremediation.⁹ Following the death of the organism, most of the body structure can be used as solid biomass to prepare biosorbents such as saw dust^{10,11} potato husk,¹² rice

The other biological systems such as human hair, human nails have been used for analysis of heavy metals poisoning as they tend to trap and concentrate these metals and other chemicals.^{17,18} Apart from the above mentioned types of adsorbents, human hair has also been used to absorb heavy metals.¹⁹ The ability of hair to bind metals is due to the keratin proteins that contain nitrogen, oxygen and sulphur all possessing high electron density.²⁰ The adsorption of Pb^{2+} and Zn^{2+} from aqueous solutions by human hair has been found to be endothermic and spontaneous process.²¹ A recent study showed that a perm-lotion-treated hair binds ions more strongly than a natural hair.²²

This manuscript presents the study the dynamics of adsorption of copper(II) ions on human hair using simple conductivity and pH measurements. The study was aimed at exploring the applicability of these simple measurements in studies of metal analyses. However the results obtained as reported herein were astounding as they revealed the nature of the interaction being not a simple chemisorption that was expected but rather a combination of this and ion exchange process. This, to the best knowledge of the authors, is the first time that such simple approach is used for such studies; as well as determining the type of interactions of the metal ions with human hair.

Experimental

Reagents and apparatus used

Anhydrous Copper Nitrate (AR) was obtained from [brand, City and Country] and used as a stock solution using distilled water. Sulphuric acid [ACE, Johannesburg, South

Africa] was used to treat the hair. Amberlite CG-50, No. A-3894 Wet Mesh 100-200 (SIGMA-Aldrich, Johannesburg, South Africa) was used in place as an alternate sorbent for comparison of the adsorption behaviour of the ions on hair.

Preparation of the adsorbent (human hair)

The sample of human hair with average length of 5 mm was obtained from one of the researchers (black African). This sample was washed with distilled water followed by ethanol to remove surface oils. Thereafter it was soaked in 10% v/w of H₂SO₄ acid for a period of one hour to remove any surface metal ions. Then it was rinsed with distilled water until the conductivity of the rinsing water becomes less 10 $\mu\text{S cm}^{-1}$ and the hair was dried in the oven 130 °C. Portions of 1g of dried hair sample were used as adsorbent at room temperature. These portions were suspended in the solution of copper ions for the requisite time and the conductivity and pH of the supernatant liquid measured appropriately.

Measurements of conductivity and pH of the solutions

An HI 8033 Hanna conductivity meter (HANNA Instruments, Romania) was used to measure conductivity. The probe of the conductivity meter was submerged in 50 mL aliquots of the 100 ppm Cu²⁺ solution and allowed to equilibrate for about 15 seconds before the reading was recorded. A longer equilibration time could not be allowed as it would affect the time dependent measurements. The pH were measurements were made with a Hanna pH-meter (HANNA Instruments, Romania) with an average 15 seconds equilibration time as well.

Quantitative analysis of copper uptake by human hair using AAS spectrometer

Different copper standard solutions were prepared and their absorbances measured using Spectra AAS 100 Spectrometer (Varian, USA) to determine correlation of absorbance to the concentration of the copper ions in the concentration range of 50–150 ppm. Thereafter, a suspension of hair and copper solution was made by suspending 10 g of hair in 500 mL of the 100 ppm Cu²⁺ solution. The supernatant solution was drawn using a pipette every 30 minutes to measure absorbances. The remaining solution was replaced immediately after the analyses.

Results and Discussions

Determination of conductivity of the copper solution after suspended of human hair

As a preliminary experiment, it was prudent to assess the degree of correlation between conductivity and concentration of Cu²⁺. To this end, the conductivity of 50 mL aliquots of Cu²⁺ ion at concentration range 100 to 500 ppm was measured at 25 °C using conductivity metre. These data demonstrated significant correlation with regression coefficient (R^2) value of 0.9637.

To assess the uptake of the Cu²⁺, 1 g of pre-treated hair was suspended in 50 mL of a 100 ppm solution for 30 minutes following which the conductivity of the supernatant liquid was measured and compared to the initial conductivity. The conductivity seemed to increase contrary to the expectation of a decrease. Further measurements were taken after 60, 90 and 120 min and the increase was consistent. Subsequently, a time-dependence profile was determined for between 30 and 120 min (Figure 1).

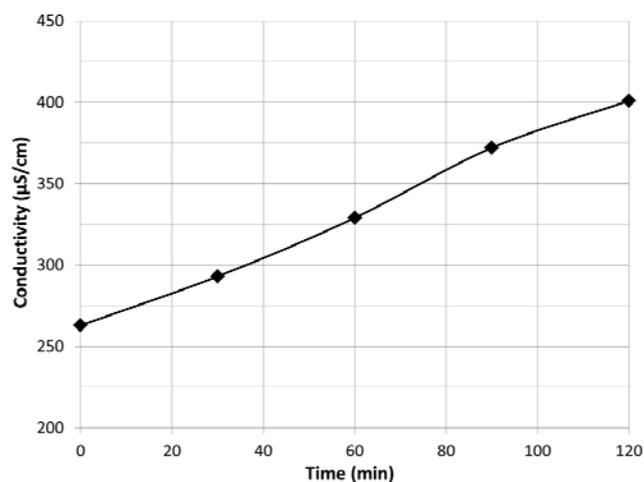


Figure 1. The plot of conductivity of solution suspending hair against time

Consistently, these results confirmed that conductivity does increase with time, implying that as more Cu²⁺ ions are taken up, conductivity increases. This was startling since conductivity would have been expected to drop as the number of ions is depleted through the adsorption process. This led to the thinking, perhaps the adsorption could be due to some ion exchange behaviour. This would explain the observed increase in conductivity being due to the release of more conducting ions as Cu ions are being adsorbed.

Correlation between conductivity to pH of the copper solution in the hair suspension

Suspecting that the increase K is due to the release of hydrogen ions, it was prudent to determine difference of [H⁺] in the resulting solution. The experiment was repeated again and this time both conductivity and pH were measured simultaneously. Figure 2 shows the combined results obtained by measuring conductivity and the pH of the solution as the time allowed for hair to remain in suspension increases. While the conductivity of the solution increases, the pH of the solution decreases simplifying the increase in H⁺ ions in the supernatant solution.

Assessment of correlation between conductivity and [H⁺] yielded a somewhat logarithmic behaviour (see Figure 3). However as expected, the plot of concentration of hydrogen ions as a function of pH resulted in a significantly linear ($R^2 = 9805$).

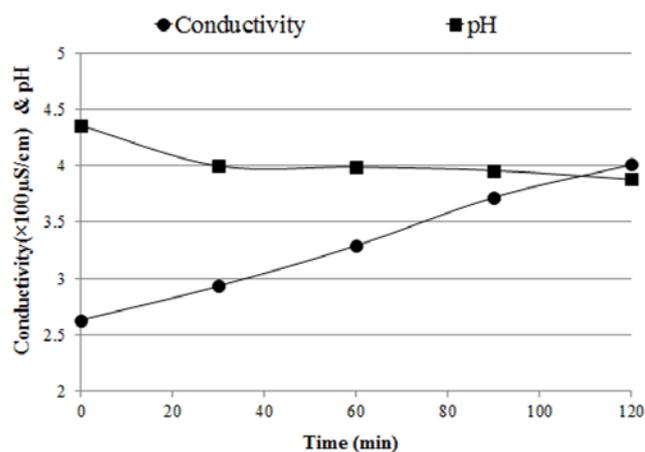


Figure 2. Conductivity and pH of the supernatant solution as a function of suspension time in human hair

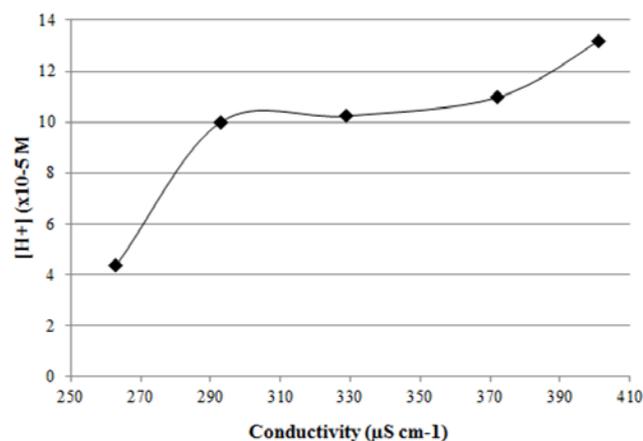


Figure 3. The plot of conductivity against concentration of hydrogen ions released

Quantitative determination of Cu²⁺ uptake by AAS

The consistent increase in conductivity led to the thought that perhaps Cu²⁺ ions were not being taken up by the hair sample, so the quantitative analysis was performed using atomic absorption spectrophotometry. Figure 4 shows the combined absorbance and the Cu²⁺ ions uptake as well as the relative concentrations. The absorbance values noted are the actual values obtained from the spectrophotometer. The relative mass uptake was taken as a difference in the mass of Cu²⁺ in solution at any time relative to $t=0$ which was taken as unity. The actual mass uptake ranged from 171 µg g⁻¹ (at $t=30$ min) to 288 µg g⁻¹ (at $t=480$ minutes, 8 h) as demonstrated in Figure 5.

As can be seen there is significant complementarity between the relative concentration of the remaining solution and the relative mass uptake. The lower amounts of copper ions uptake (micro-gramme range) could be due to the poor optimisation of the hair such as carrying out static instead of dynamic equilibration. Since no quantitative checks were made to rid the hair of any pre-trapped metal ions was performed, it could be that the sample already had a significant amounts of other metal ions that competed with the analyte.

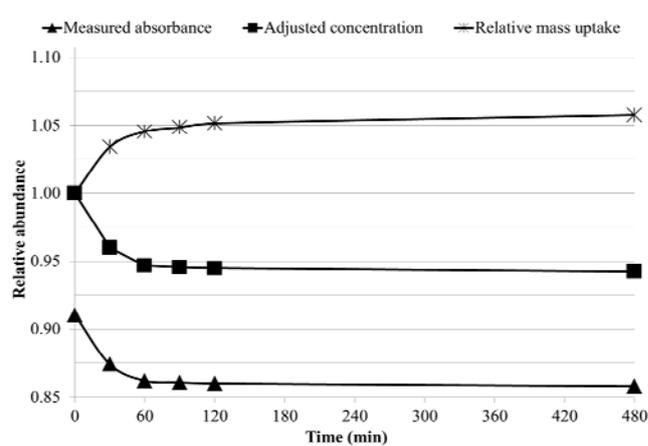


Figure 4. Measured absorbance, adjusted concentration and relative Cu²⁺ uptake

The other issue could be the fact that the hair was not ground into a fine powder but was rather used as short strands of about 5 mm length. This is consistent with the report that the hair sample treated with mineral acids can be soaked up to 48 h but do not show considerable “softening of the fibres” and hence “exhibit negligible adsorption capacity for Cu²⁺ [ions]” below 0.1 mg g⁻¹ of hair.²³

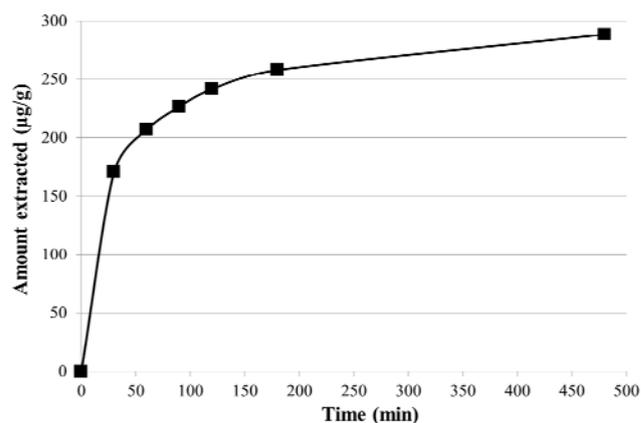


Figure 5. A plot of Cu²⁺ uptake as a function of time

However, a similar trend of the Cu²⁺ ions uptake was observed and reported earlier.²¹ In the same report, it was stated that the isoelectric point of human hair is 3.67 indicating a high proton exchange above this pH value. Thus, as the pH decreases (increase in H⁺ ions) due to ion exchange behaviour, less and less Cu²⁺ ions are taken up. The absence of correlation between the conductivity, Cu²⁺ uptake and pH suggests a complex ion exchange process between Cu²⁺ ions and H⁺ ions.

From the appearance of the plot of [Cu²⁺] with time (Figures 4 and 5), it seems likely that the uptake follows the first order kinetics, where the concentration at anytime t is exponentially related to time expressed mathematically as follows:

$$C_t = C_0^{-kT} \quad (1)$$

Implying that:

$$\ln C_t = -kT + \ln C_0 \quad (2)$$

Thus a plot of $\ln C_t$ against time should yield a straight line whose slope equals the rate constant and the y-intercept equalling the $\ln C_0$. However, the plot yielded a regression coefficient of 0.4455 and a regression equation:

$$y = 0.8839e^{-8E-05x} \quad (3)$$

demonstrated a deviation from a first order kinetics.

Determination of ion exchange behaviour of hair compared to Amberlite

Determining the possibility of ion exchange process being involved in the adsorption of copper ions by human hair, the suspension of Amberlite was prepared and both conductivity and pH measured and compared as in Figure 6.

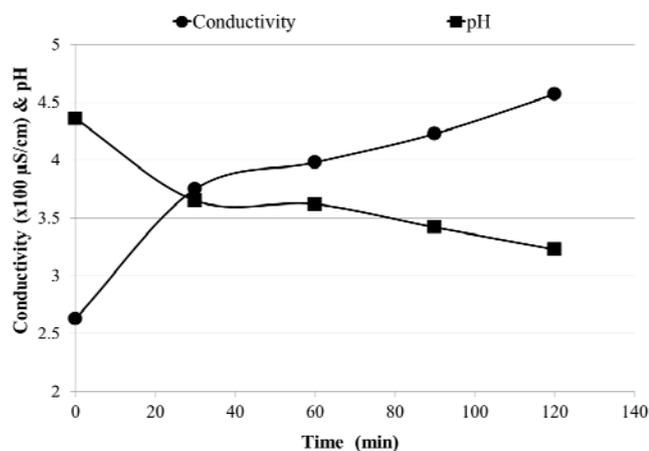


Figure 6. Conductivity- and pH-time profile of the supernatant solution suspended in Amberlite

Unlike the case of human hair, the conductivity versus pH curve yielded a sufficiently linear curve ($R^2 = 0.9926$) indicating the positive correlation between conductivity and the pH of the supernatant solution, hence abundance of the H^+ ions.

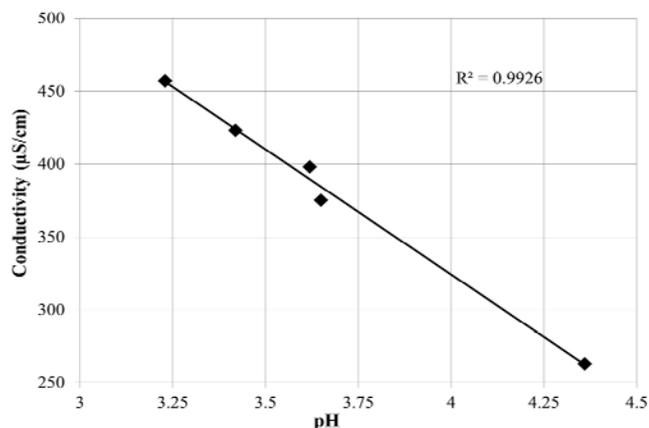


Figure 7. The correlation of measured conductivity and pH for Amberlite suspensions

Comparison of the pH and conductivities of suspensions of hair and Amberlite showed that more H^+ ions were liberated using the Amberlite than using the human hair (See Figure 8).

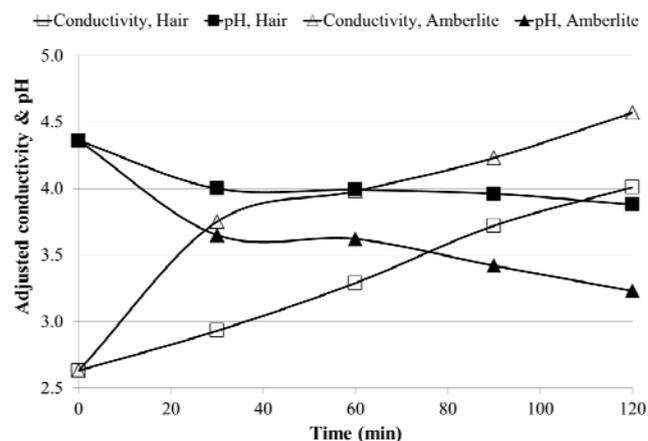


Figure 8. Comparison of conductivity and pH for Amberlite and human hair suspensions

These different behaviours suggest a complex mechanism of adsorption exist in hair than in Amberlite which is both chemisorption and ion exchange in nature. The correlation of conductivity with pH in the case of Amberlite resin (Figure 7) shows a linear relationship contrary to the case with the human hair (Figure 3). Since no quantitative analysis of Cu^{2+} ions was performed for Amberlite, no inference can be made to the concentrations of the two ions, the H^+ and the Cu^{2+} ions. However, one study revealed that Cu^{2+} could get as high as 115 mg g^{-1} when the Amberlite IR 120 is packed in a cartridge and the pH adjusted optimally.²⁴ However the pH of the solution could not be optimised since the activity of H^+ ions was the focus of the study. The conclusion of the ion exchange behaviour is affirmed by the report that the human hair “could be used as a cation-selective adsorbent, as it showed no capacity for removing anions”.²²

Conclusions

In conclusion, this study revealed very interesting aspects that were not envisaged that conductivity studies could reveal so much detail regarding metal uptake by sorbents. The adsorption of Cu^{2+} copper ion on human hair was found to be a combination of chemisorption and ion exchange with a maximum observed at 288 μg g^{-1} of hair. The chelation process occurs between the Cu^{2+} ions and the electron-rich nitrogen, sulphur and oxygen atoms of the hair proteins (keratin). The uptake does not follow the first order kinetics as would be expected from a simple chemisorption process, although the plot of the uptake versus equilibration time demonstrates a logarithmic increase. This ion exchange process is not an easy straightforward cation exchange as that observed with a simple classical ion exchange resin like Amberlite. Further experiments are needed to decipher the full mechanism of this process and full quantitative analysis for all other elements that could be playing different roles in the whole process.

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