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Adsorption of heavy-metal ions (Pb^{2+}, Cu^{2+}) on perm-lotion-treated human hair

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Abstract−Removal of toxic heavy metal ions from environmental and biological systems is important, but the use of commercially available heavy metal adsorbents is complicated by the need for specific pretreatment steps. We chose to study human hair treated with perm lotion as a heavy metal adsorbent because it is readily available and contains a large number of sulfur atoms for strong coordination to heavy metal ions. The optimal pH of adsorption by perm lotion-treated human hair was 4.16, which was slightly higher than the isoelectric point (pI) of the hair. The maximum removal ratio at pH 4.16 was 88.5% for a 50 ppm Cu^{2+} solution, and 96.79% for a 50 ppm Pb^{2+} solution. Almost 90% of the Pb^{2+} was removed from a 120 ppm Pb^{2+} solution. The perm-lotion-treated human hair was a cation-selective adsorbent.

Keywords: Human Hair, Heavy Metal, Adsorption

INTRODUCTION

Heavy metal ions are the main components of industrial wastewaters that pollute and destroy the environment. Ingestion of heavy metal ions by animals is a serious problem, as these elements are not easily excreted. Human beings consume many animals that ingest these contaminants (cows, fish, etc.); therefore, heavy metal contamination of animals directly affects human health. For instance, Japan experienced the Minamata tragedy and Itai-Itai disease because of the human consumption of mercury contaminated fish and cadmium contaminated rice, respectively. Many countries have now introduced laws that impose limits on the release of heavy metal ions into aquatic systems. Therefore, removal of heavy metal ions from wastewater is an important area of research for maintaining human health and the environment.

Several methods are available for the removal of heavy metal ions from aqueous solutions, including adsorption methods (using activated carbon, zeolites, and agricultural wastes) [1-3], ion-exchange [4], precipitation [5], and biosorption [6]. Among these, adsorption is favored in industrial settings. Some adsorbents are relatively expensive, while others, such as artificial and natural zeolites, require involve additional processing steps [7] or pretreatments [2] prior to usage.

Our aim was to identify an effective and economical adsorbent for heavy metal removal from water. Human hair has long been known to have a strong capacity for heavy metal adsorption for several reasons. First, tiny cracks exist on the surfaces of human hairs that can facilitate the physical adsorption of heavy metal ions to the hair surface. Second, the long peptide chains in a human hair contain unshared electron pairs in atoms such as oxygen and nitrogen. These electron pairs can coordinate to heavy metal ions, thereby facilitating chemical adsorption of those ions onto the hair surface. Finally, human hair has a high proportion of sulfur-containing cysteine (Cys) amino acids, which can strongly coordinate to heavy metal ions, thereby strengthening chemical adsorption onto the hair.

Hong et al. (2008) reported the adsorption of heavy metal ions ($Cr_2O_7^{2-}$, Cu^{2+}, Cd^{2+}) by human hair [11] treated with HCl, NaOH, H_2O_2, and CH_3COOH to increase physical adsorption. However, the maximum removal ratios were quite low for 10 ppm aqueous solutions: 35.8% ($Cr_2O_7^{2-}$), 17.1% (Cu^{2+}), and 36.8% (Cd^{2+}). Heavy metal adsorption to hair involves interaction with cysteine amino acids; these are connected via disulfide bonds so that the sulfur atoms can coordinate to the heavy metal ions (Fig. 1). However, if the disulfide bonds are reduced to mercapto (-SH) groups, the sulfur atoms can more readily coordinate to the heavy metal ions, as shown by Dąbrowski et al. [4], who studied the removal of mercuric ions (Hg^{2+}) using -SH groups. Therefore, we examined the efficiency of heavy metal adsorption by human hair following reduction of the hair disulfide bonds with perm lotion and 2-mercaptoethanol (ME). We also examined the effects of pH and initial concentration on the removal ratio for Pb^{2+} and also determined the removal ratios for Cu^{2+} and $Cr_2O_7^{2-}$ to establish the effect of the ion charge (i.e., negative or

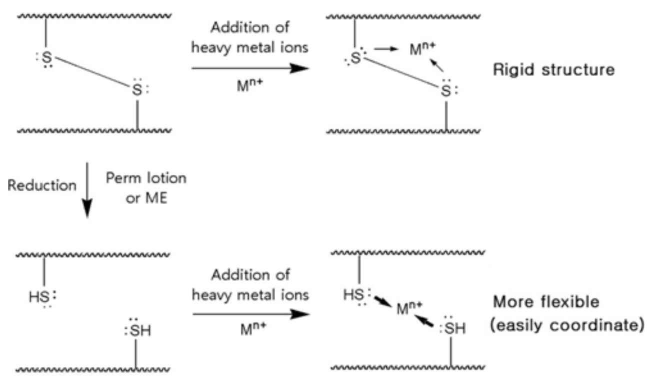

Fig. 1. Reduction of human hair and heavy-metal-ion removal.

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positive) on heavy metal adsorption.

EXPERIMENTAL

1. Materials

Three separate 1,000 ppm solutions of Pb^{2+}, $Cr_2O_7^{2-}$, and Cu^{2+} were prepared using $PbCl_2$ (DaeJung Chemicals, >98%), $CuSO_4\cdot 5H_2O$ (Kanto Chemical Co., >99.5%), and $K_2Cr_2O_7$ (Shinyo Pure Chemicals, >99.5%). The solutions were then diluted to 20-120 ppm for usage. A large quantity of human hair was sourced from a hair salon (Leeminhair: 495-13, Songjuk-dong, Jangan-gu, Suwon-si, Gyeonggi-do, Republic of Korea). The hair was rinsed with detergents, washed with deionized water, and then dried at room temperature. Perm lotion (Avangadro) and 2-mercaptoethanol (DaeJung Chemicals, >99.0%) were purchased for reducing the disulfide bonds in the hair.

2. Reduction of Disulfide Bonds

For the perm lotion treatment, the hair was spread out on a wide glass plate and then mixed with an excess amount of the perm lotion. For the ME treatment, 10 g of hair, 50 mL of deionized water, and 50 mL of ME were mixed in a 250 mL beaker. Because the reduction of disulfide bonds by ME is accelerated in basic conditions [17], hair was reduced by four different methods by adding 100 mL of each of the following solutions to the mixture: 0.200 M $HCl_{(aq)}$ (Duksan Chemicals, 35-37%), 0.200 M $NH_4OH_{(aq)}$ (DaeJung Chemicals, 25-28%), 0.200 M $Na_2CO_{3(aq)}$ (Duksan Chemicals, >99%), 0.200 M $NaOH_{(aq)}$ (Duksan Chemicals, >93%).

3. Preparation of Heavy Metal Solutions

The pH of the heavy metal solution was controlled by replacing $1/8^{th}$ of the total volume of the diluted solution with a buffer solution. The pH of the solution was accurately measured by adding a few drops of 5 M HCl and NaOH solutions while simultaneously measuring with a pH sensor (Vernier). The removal ratio of the human hair was highest at pH 4.16; therefore, the experiments were performed at that pH unless otherwise stated.

4. Measurement of Removal Ratios

The removal ratios of the hair were measured by a batch adsorption method [1,2] using plastic bottles and a magnetic stirrer (WiseStir MSH-20D, Witeg, Germany). First, a diluted heavy metal solution was poured into a bottle. The temperature of the solution was maintained at 25 °C in a circulating constant temperature bath (WiseCircu WCH-12, Witeg, Germany). Once thermal equilibrium was reached, the adsorption tests were performed by stirring the solution at 300 rpm. The efficiency of the perm-lotion-treated human hair was compared with other commercially available adsorbents by maintaining the ratio between the human hair and the heavy metal solution at 0.75 g: 160 mL, respectively. Fig. 2 shows the experimental setup.

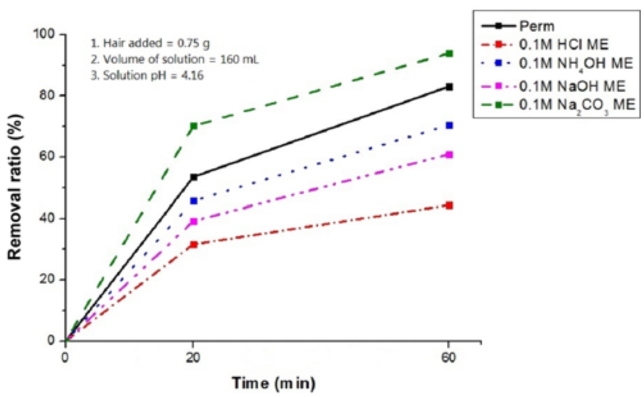

Fig. 2. Removal ratio for Pb^{2+} from reduced human hair by various reducing methods (30 ppm Pb^{2+}).

Samples of the heavy metal solution were collected from the plastic bottles at five equal time intervals (4 min). In some experiments, the time interval was changed to 2 min or additional samples were collected, depending on the intended tests. The samples were filtered through 45-μm syringe filters (SRC045025H, Chemlab, Spain) to separate the adsorbents from the solution, and the filtrates were collected in vials. The heavy metal removal ratio of the human hair was calculated using the following equation:

$$p=(C_0-C)/C_0\times 100\ (\%)$$

p: heavy metal removal ratio of the human hair
C_0: initial concentration of the solution
C: concentration of the final solution

The concentrations of Pb^{2+} and Cr^{6+} were measured by atomic absorption spectroscopy (AAS) (AAnalyst 400, Perkin Elmer, USA), while the concentration of Cu^{2+} was measured by iodometric titration [18]. The AAS samples were first diluted to 2-10 ppm prior to measurement. A calibration curve for AAS was constructed by measuring the intensity of the 2 ppm and 10 ppm heavy metal standard solutions. The concentrations of the diluted samples were then determined based on this calibration curve.

5. Field Emission-scanning Electron Microscopy (FE-SEM) and Pyrolysis-GC Analyses

The surface structure of the human hair was analyzed using the FE-SEM (JSM-6700F, Jeol, Japan) to determine structural changes that could explain differences the hair's adsorption efficiency. The forms of sulfur atoms in the hair were analyzed based on the Pyrolysis-GC (gas chromatography) (MSO-GCMS, Agilent, USA) graph of the hair. The sum of the peak areas was calculated for molecules that contained sulfur atoms (A) and molecules that contained -SH groups (B). The proportion of sulfur atoms in the form of -SH groups was calculated by dividing B by A.

RESULTS AND DISCUSSION

1. Effect of Various Reduction Methods on Pb^{2+} Removal

Fig. 2 shows the removal ratio for Pb^{2+} in a 30 ppm solution at pH 4.16 by human hair reduced by perm lotion or ME. The samples were collected at intervals of 20 and 60 min after the adsorption started. The ME treatment was more effective in basic conditions because the sulfur atoms in ME needed to be converted to the thiolate forms in order to reduce the disulfide bonds in the hair [18] (Fig. 3). The treatment with ME and Na_2CO_3 resulted in hair with the highest adsorption efficiency. However, perm lotion was more readily available than ME, so subsequent tests were performed using hair treated

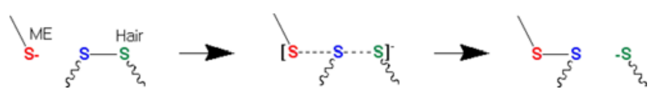

Fig. 3. Reduction mechanism of disulfide bonds.

with perm lotion.

2. Effect of Disulfide Bonds Reduction on Pb^{2+} Removal

Fig. 4 shows the removal ratios for the perm-lotion-treated and non-treated hair immersed in a 20 ppm Pb^{2+} solution. Samples were collected at time intervals of 2 min each for 10 min.

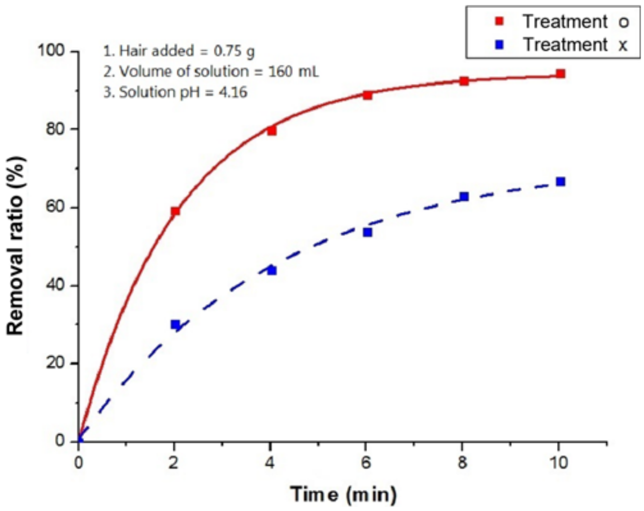

Fig. 4. Removal ratio for Pb^{2+} from perm-lotion-treated and non-treated human hair (20 ppm Pb^{2+}).

The removal ratio of the perm-lotion-treated hair was 94.35% at 10 min, while that of the non-treated human hair was 66.74%; i.e., perm lotion treatment increased the removal ratio for Pb^{2+} by 27.61%. Kang et al. showed that the removal ratios of zeolite and bentonite in a 20 ppm Pb^{2+} solution after 24 h were 99.1% and 91.6%, respectively [12]. Similarly, Netzer et al. showed that removal ratios of ten different commercialized activated carbons in a 10 ppm Pb^{2+} solution were below 92% after 2 h [13]. Therefore, perm-lotion-treated hair was a relatively better heavy metal adsorbent compared to these commercially available adsorbents. Fig. 5 shows the FE-SEM images of the untreated and perm-lotion-treated hair. The surface of the non-treated hair is very smooth, whereas the perm-lotion-treated hair shows many surface cracks. It is likely that the perm lotion treatment increased the surface area, and hence the physical adsorption onto the hair. Fig. 6 and Table 1 show the proportion of sulfur atoms existing in the form of -SH groups on the non-treated and perm-lotion-treated hair. The perm lotion treatment increased the proportion of -SH groups from 17.31% to 26.78%, supporting the idea that the hair's ability to remove heavy metal ions increased with the increasing proportion of -SH groups.

The report by Wilson et al. on the cysteine content of human

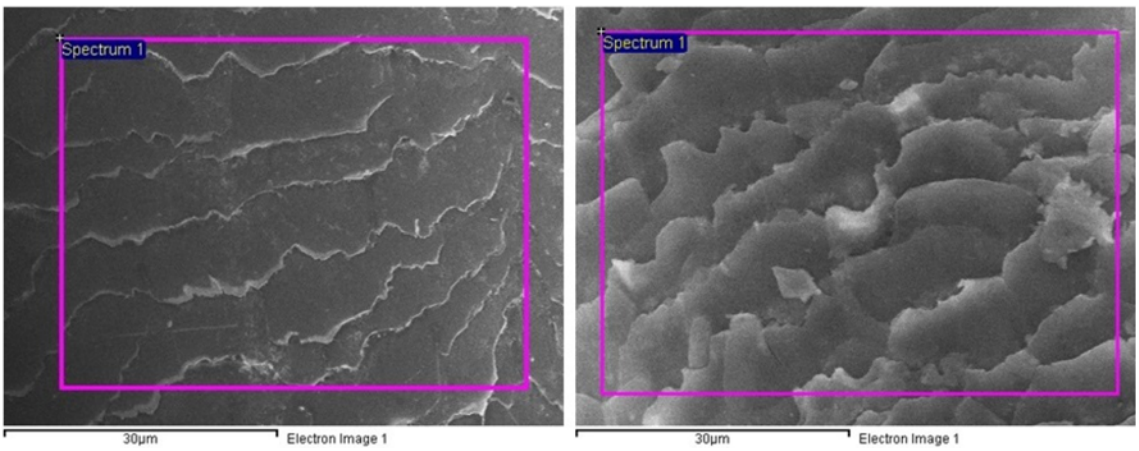

Fig. 5. FE-SEM images of non-treated (left) and perm-lotion-treated hair (right).

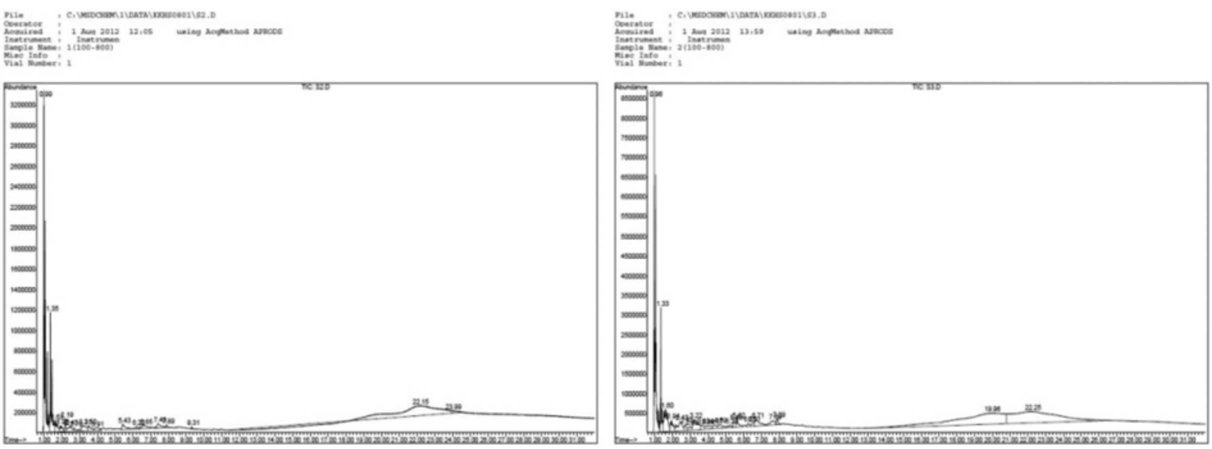

Fig. 6. Pyrolysis-GC analysis of non-treated (left) and perm-lotion-treated hair (right).

Table 1. Determination of proportion of -SH groups in hair

Entry	Total S[a] (A)	SH[b] (B)	B/A 100 (%)
Non-treated hair	8,955,954	1,548,302	17.31
Perm-lotion-treated hair	39,963,509	10,704,473	26.78

[a]Sum of areas of molecules containing sulfur atoms
[b]Sum of areas of molecules containing -SH groups

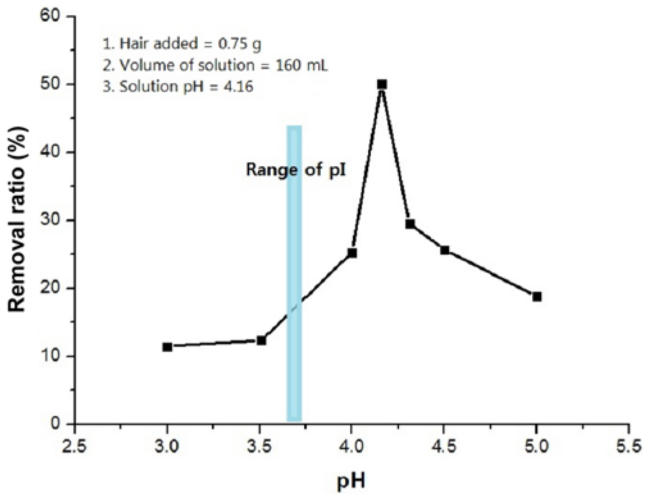

Fig. 7. Removal ratios of perm-lotion-treated hair at different pH values (35 ppm, Pb^{2+}).

(17.6%), dog (19.0%), and cat (13.1%) hair [10] indicated that animal hair also contained a relatively large proportion of sulfur atoms. Therefore, animal hair could potentially adsorb heavy metal ions in the same fashion as was observed in the present study for human hair.

3. Effect of pH on Pb^{2+} Removal

Heavy metal ions compete with protons (H_3O^+) for coordination to human hair. Hence, the pH of the heavy metal solution will affect the removal ratio. Fig. 7 shows the removal ratio of Pb^{2+} from a 35 ppm solution by the perm-lotion-treated hair at various pH values after 20 min.

The removal ratio was the highest at pH 4.16; it decreased when the pH was either above or below 4.16. This may be a reflection of the isoelectric point (pI) of the human hair; previous studies reported the pI to be 3.67 (Jachowicz et al.) and 3.70 (Vernon et al.) [8,9]. As seen in Fig. 8, the surface charge of the human hair is positive when the pH is below the pI, and negative when pH is above the pI [17]. The removal ratio increased with increasing pH up to pH 4.16, because the electronic attraction between the heavy metal ions and the human hair increased. However, above pH 4.16, the removal ratio decreased because of the precipitation of $Pb(OH)_2$ owing to the increased availability of hydroxide ions (OH^-).

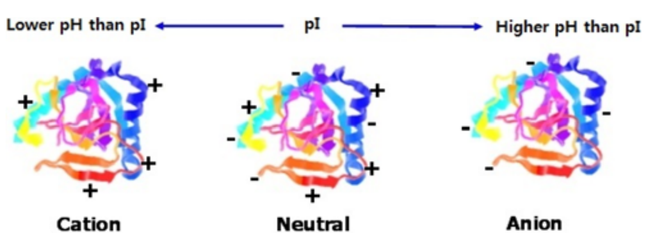

Fig. 8. Surface charge of human hair and pI.

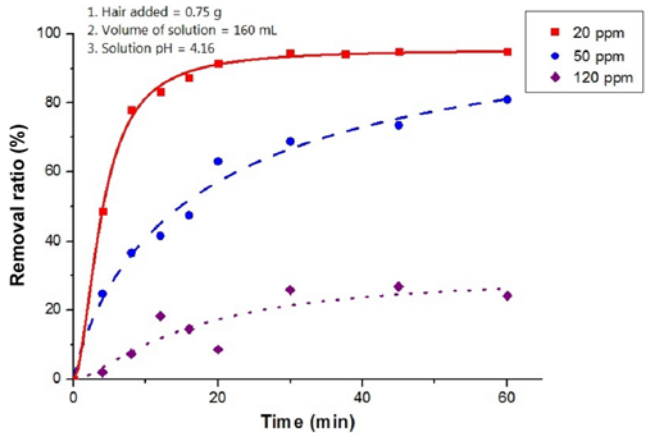

Fig. 9. Removal ratios of perm-lotion-treated hair in solutions of different initial Pb^{2+} concentrations.

Table 2. Removal ratios of perm-lotion treated-hair in solutions of different initial Pb^{2+} concentrations

Initial Pb^{2+} concentration (ppm)	Removal ratio after 1 day (%)	Removal ratio after 2 days (%)	Removal ratio after 3 days (%)
20	94.72	-	-
50	96.79	-	-
120	75.62	84.98	89.02

4. Removal of Pb^{2+} from Solutions of Different Initial Concentrations

Fig. 9 shows the removal ratios for the perm-lotion-treated hair in solutions with different initial Pb^{2+} concentrations. The samples were collected at time intervals of 4 min each for 20 min and additional samples were collected after 30, 45, and 60 min and after 1, 2, and 3 days.

The removal ratio was highest for the 20 ppm Pb^{2+} solution and lowest for the 120 ppm Pb^{2+} solution. Interestingly, the removal ratio was 94.35% after 20 min for the 20 ppm Pb^{2+} solution.

Table 2 shows the removal ratios after 1-3 days of adsorption. The 50 ppm Pb^{2+} solution had a removal ratio of 96.79% after 1 day, while the 120 ppm Pb^{2+} solution had removal ratios of 84.98% and 89.02% after 2 and 3 days, respectively. Therefore, we inferred that the perm-lotion-treated hair could efficiently remove Pb^{2+} ions even from a highly concentrated solution.

5. Effect of Ionic Charge on Removal of Heavy Metals

The results obtained for cation (Pb^{2+}) removal were compared with results for heavy metal anion ($Cr_2O_7^{2-}$) removal. Fig. 10 shows the concentration of Cr^{6+} in the solution. The adsorption was performed over the pH range 4.5-10 and samples were collected at time intervals of 4 min each for 20 min. No removal of $Cr_2O_7^{2-}$ was observed at any pH value.

This experiment was then repeated with a cation, Cu^{2+}. As shown in Table 3, the removal ratio for Cu^{2+} was 88.5% (50 ppm) and 46.5% (120 ppm) after two days of adsorption, which indicated that the perm-lotion-treated hair was able to remove Cu^{2+} cations. Thus, perm-

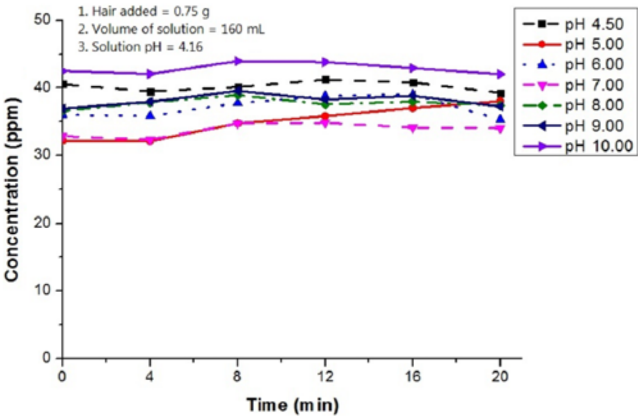

Fig. 10. Change in concentration of Cr^{6+} in solution (Cr^{6+}, 40 ppm).

Table 3. Removal ratios of Cu^{2+} inperm-lotion-treated hair

Initial concentration of Cu^{2+}(ppm)	Removal ratio after 1 hour (%)	Removal ratio after 1 day (%)	Removal ratio after 2 days(%)
50	24.0	73.5	88.5
120	11.3	32.9	46.5

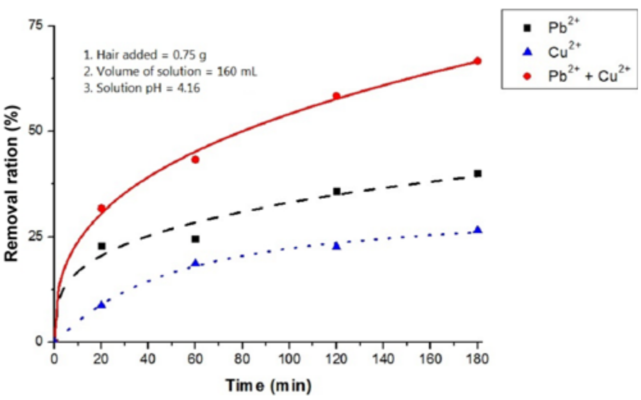

Fig. 11. Removal ratios of perm-lotion-treated hair in a mixed-heavy-metal solution (Pb^{2+}=Cu^{2+}=40 ppm).

lotion-treated hair could be expected to be useful as a cation-selective heavy metal adsorbent.

6. Removal Ratio of Hair for a Mixture of Heavy Metals

Fig. 11 shows the removal ratio of the perm-lotion-treated hair from a heavy solution containing a mixture of heavy metals (Pb^{2+}=Cu^{2+}=40 ppm). A substantially larger amount of Pb^{2+} than Cu^{2+} was in agreement with the earlier results. The sum of the two ratios was 66.67% after 3 h of adsorption, which meant that the perm-lotion-treated hair could also remove heavy metal ions from a mixture. However, the sum of the ratios was smaller than that obtained with Pb^{2+} alone.

CONCLUSION

The paper confirmed the ability of human hair to adsorb heavy metal ions due to the presence of reduced disulfide bonds. Treatment of hair with a mixture of ME and Na_2CO_3 resulted in the highest removal ratio. The removal ratio for hair treated with perm lotion was slightly lower than that observed with ME, but the ready availability of perm lotion made this treatment preferable. The perm lotion treatment increased the removal ratio of the hair by 27.62% at 20 ppm Pb^{2+}. The removal ratio of the perm-lotion-treated hair was maximal at pH 4.16. The perm-lotion-treated hair satisfactorily removed heavy metal ions from solutions with high concentrations; e.g., 89.02% of the Pb^{2+} was removed from a 120 ppm solution after three days. In summary, perm-lotion-treated human hair could be used as a cation-selective adsorbent, as it showed no capacity for removing anions such as $Cr_2O_7^{2-}$.

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