Adsorption of Heavy Metal Ions Using Recycled Cellulose from Newspaper

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Abstract

The issue of water pollution is jeopardising our health. Many pollutants in water harm the health of humans, including metals. Therefore, this study aims to come up with a cost-efficient and environmentally-friendly method to remove heavy metal ions in water. The study mainly consists of 4 stages. Firstly, Cellulose was extracted from the waste newspaper. The Cellulose collected was then chemically modified to increase its absorbency. A heavy metal ion absorbance test was then conducted to find out which Cellulose has the highest absorbency. Following that, the heavy metal ions were removed, and the Cellulose was regenerated for further use. A heavy metal ion test was conducted again to see the change in the absorbency of the cellulose. Cellulose treated with citric acid was found to have the highest absorbance of Zinc ions and Iron (III) ions, while cellulose treated with EDTA was found to have the highest absorbance of Copper (II) ions.

Introduction

There has been a growing concern about the issue of water pollution. Water pollution is causing many deaths each year, more than war and all other forms of violence combined. (Fuller et al., 2017). One such pollutant of water is metals. Metals are introduced in aquatic systems as a result of the weathering of soils and rocks, from volcanic eruptions, and from a variety of human activities involving the mining, processing, or use of metals and/or substances that contain metal pollutants. For example, most common metal pollution in freshwater comes from mining companies. They usually use an acid mine drainage system to release heavy metals from ores, because metals are very soluble in an acid solution. When the acid solution is dispersed in the groundwater, containing high levels of metal ions in the

acid solutions. When people drink polluted waters, toxic amounts of heavy metals enter the body and accumulate in the tissues, and the resulting poisoning can cause serious damage. It causes many serious health problems and water-borne diseases like cholera and kidney damage (Fazal-Ur-Rehman, M., 2018).

Over the years, several techniques have been developed to remove heavy metals from the environment, such as ion exchange, adsorption, reverse osmosis, electrolytic reduction, precipitation, and solvent extraction (Hubicki & Kołodyńska, 2012). However, most of these techniques are either expensive or energy-demanding. This study investigates a method that would be more cost-efficient and more environmentally friendly, to remove heavy metal ions in water.

Objectives and Hypotheses

This study aims to:

1. Extract cellulose from newspaper using methods such as bleaching
2. Chemically modify the cellulose such that it can adsorb the maximum amount of heavy metal ions
3. Study the adsorption of heavy metal ions with modified and unmodified cellulose
4. Recycle and regenerate the used cellulose

This study hypothesises that:

1. Newspaper can be bleached to extract its cellulose content
2. Chemically modified cellulose is able to adsorb a higher content of metal ions as compared to unmodified cellulose
3. The used cellulose is able to be recycled and regenerated for further use

Methodology

Extraction of Cellulose from Newspaper

Sheets of newspaper were cut into small pieces and treated with 5% Sodium Hydroxide(NaOH) solution at 80°C for 3 hours (Figure 1). It was further treated in ethanol solution at room temperature for 3 hours, then thoroughly rinsed with deionised (DI) water for at least 6 times in order to remove any residual. It was then treated with hydrogen peroxide for 2 hours (Figure 2), before being centrifuged for 6000rpm for 5 minutes and refrigerated.

Figure 1: Small pieces of newspaper treated with 5% sodium hydroxide solution at 80°C for 3h.

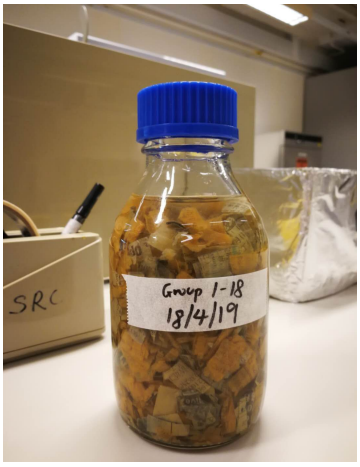

Figure 2: Cellulose treated with hydrogen peroxide for 2h.

Figure 3: After being rinsed with DI water for 6 times, the treated Cellulose was centrifuged.

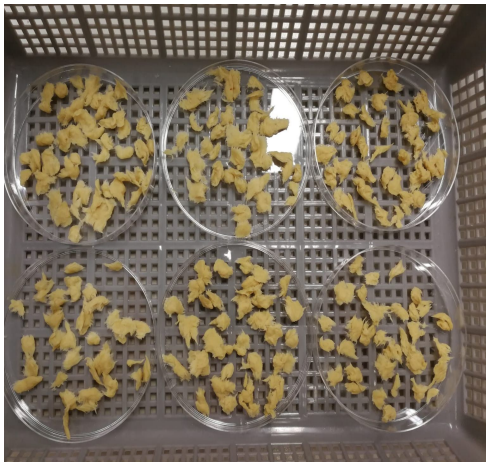

Figure 4: The resultant was then dried and refrigerated for further use.

Chemical Modification of Cellulose

Method 1: Citric Acid

0.5g of treated Cellulose was mixed with a solution of 1.5g of citric acid in 8 ml of water. The cellulose was then dried in an oven at 80°C for 5 hours. The resultant was then rinsed with DI water for 6 times before being dried. The final product was further awaited to be used as an adsorbent.

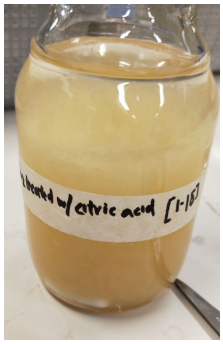

Figure 5: Cellulose treated in citric acid solution.

Method 2: Esterification

4g of Cellulose was treated in a sodium hydroxide solution and placed in a round bottom flask. 30g of acetic acid was dissolved in 300ml DI water to form acetic acid solution, while 30g of EDTA was also dissolved in another 300ml DI water to form an EDTA solution. 2g of treated Cellulose was placed in each solution for 12 hours. Both solutions are then heated at 100°C. The Cellulose was then removed from the acid solutions and placed in separate petri dishes.

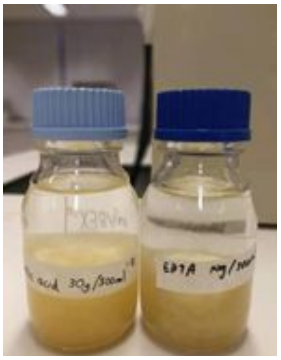

Figure 6: Cellulose treated with acetic acid and EDTA solutions.

Heavy Metal Ion Adsorption Test

Preparation of 50ppm Metal Ion Solutions

Three metal ion solutions were prepared - copper, zinc and iron. For Copper (II) Ion, 0.098g of Copper (II) Sulfate was measured and diluted in 500ml DI water. For Zinc Ion, 0.052g of Zinc Chloride was added and diluted in 500ml DI water. For Iron (III) Ion, 0.0725 of Iron (III) Chloride was added and diluted in 500ml DI water.

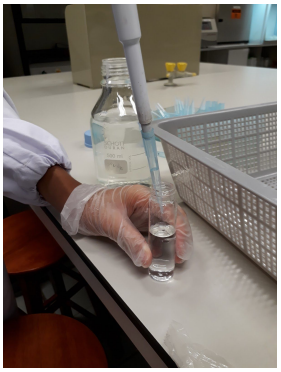

Figure 7: Preparation of Metal Ion Solutions

Adsorption Test

The ions solutions made were first tested to ensure that they were of about 50ppm. For Copper (II) Ions, 0.5 ml of the Copper (II) Sulfate solution was mixed with 19.5 ml of DI water. Copper Powder Pillows were added to 10ml of the 20ml solution made in the previous step and its concentration tested using a colourimeter. For Zinc Ions, 0.5 ml of the Zinc Chloride solution was mixed with 19.5ml of DI water, and Zinc Powder Pillows were added afterwards. The 20ml solution was split into 2 bottles of 10ml each. 0.5ml of cyclohexanone was added to one 10ml bottle and its concentration was tested using a colourimeter. For Iron (III) Ions, 0.5ml of the Iron (III) Chloride solution was mixed with 19.5ml of DI water. Iron Powder Pillows were added to 10ml of the solution and its concentration was tested using a colourimeter.

Control Cellulose (untreated), Cellulose treated with citric acid, EDTA and acetic acid respectively were put into bottles containing Iron (III) ions, Copper (II) ions and Zinc ions respectively. Each experiment was repeated 3 times, with each bottle containing 1.7g of treated cellulose. After 1 hour, the Cellulose was taken out and the ion solution was tested with the colourimeter to see the change in concentration of heavy metal ions.

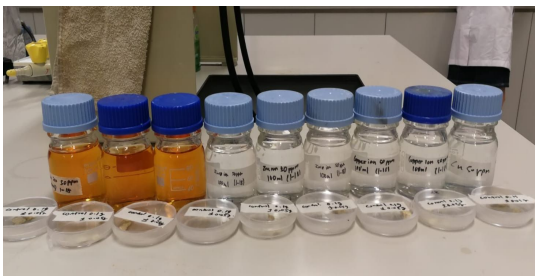

Figure 8: Copper (II), Zinc and Iron (III) ion solutions used to test untreated Cellulose, as well as cellulose treated with acetic acid, citric acid and EDTA.

Regeneration of Used Cellulose

The cellulose was treated with 1M of either HCl or NaOH. The solution consisted of 100 ml HCl/NaOH and 2.5g of Cellulose. The solutions were stirred mechanically and left to settle.

There were 2 layers formed, the supernatant and the precipitate (Cellulose). The supernatant was collected and analysed for the concentration of metal ions using a colourimeter.

Results and Discussion

Chemical Modification of Cellulose - FTIR

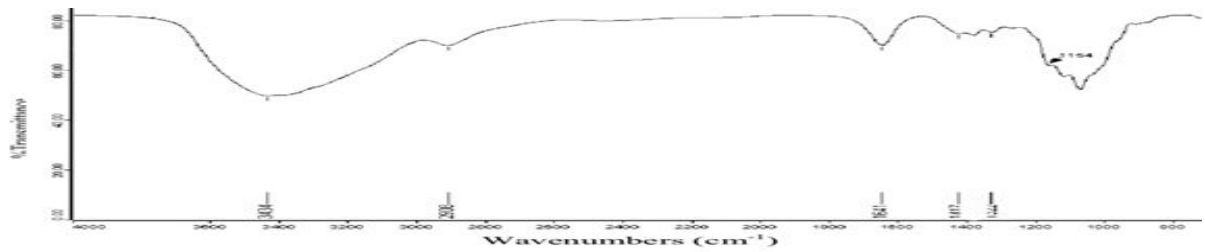

Figure 9: FTIR spectrum graph for the sample Cellulose

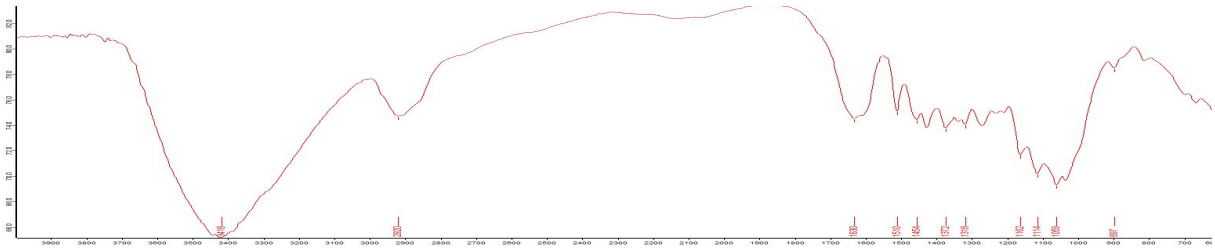

Figure 10: FTIR spectrum graph for the control set-up Cellulose

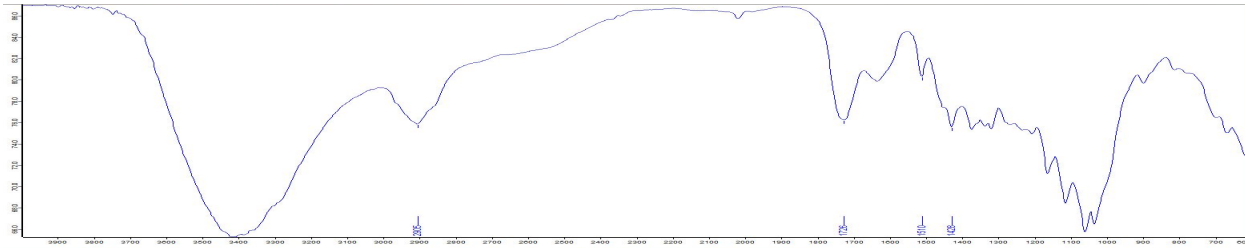

Figure 11: FTIR spectrum graph for Cellulose treated with citric acid

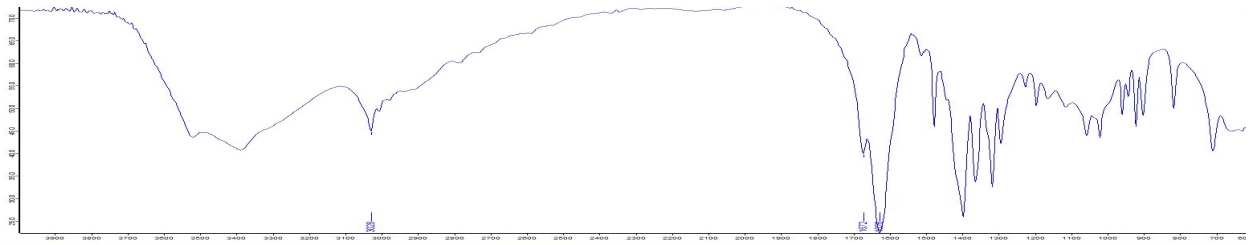

Figure 12: FTIR spectrum graph for Cellulose treated with EDTA

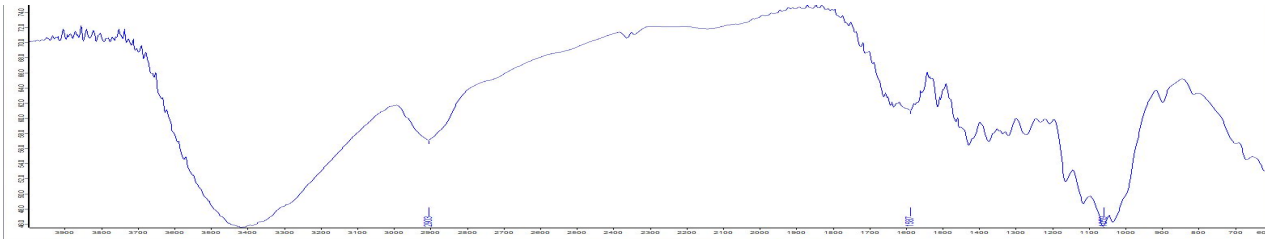

Figure 13: FTIR spectrum graph for Cellulose treated with acetic acid

The Fourier-transform infrared spectroscopy (FTIR) spectra of Cellulose fibres from newspaper treated with varying acids are compared with reference to samples tested in Figures 9. Identification of the absorption bands in Figure 10 is as follows. The broad peak at 3418 is characteristic for stretching vibration of the hydroxyl group in polysaccharides. This peak includes both inter- and intra-molecular hydrogen bond vibrations in cellulose. The band at 2920 as well as the various small peaks from 1372 to 1510 are attributed to CH stretching vibration of all hydrocarbon constituents in polysaccharides. The peaks located at 1630 correspond to the vibration of water molecules absorbed in cellulose. The peak at 900 also shows OH bending. With the results obtained from this FTIR similar to the expected FTIR of cellulose, this study has successfully extracted cellulose from newspaper.

In Figure 11, the peak at 1726 suggests CO stretching, unlike the control set-up with no peak present. This is due to the hydroxyl groups in Cellulose (OH and CH_2OH) reacting with the carboxyl functional group (CO_2H) in citric acid to form ester bonds. As compared to acetic acid in Figure 13, despite having similar functional groups, the peak in citric acid is much more

distinct than that in citric acid. This is because citric acid contains 3 carboxyl functional group and 1 hydroxyl functional group, showing that the Cellulose is able to bond with the citric acid better and can adsorb the metal ions better because of all these polar groups. On the other hand, the structure in acetic acid contains only 1 carboxyl functional group and cannot bond strongly with Cellulose.

In Figure 12, the peak at 1626 suggests CO stretching from EDTA, while the peak at around 1200 suggests CN stretching. Thus, we can conclude that the EDTA is covalently bonded with the Cellulose. The EDTA acted as a chelating agent, and we can tell as it absorbed almost all the copper, showing that the EDTA acted as a chelating agent which chelated and got rid of almost all the copper.

In Figure 13, the peak at 1700, representing C=O bond, is missing, thus showing that acetic acid has not chemically bonded with Cellulose. Since acetic acid only contains 1 carboxyl functional group, it is unable to bond so well with the hydroxyl functional groups in cellulose. With reference to the results collected, the absorbance of the Cellulose treated with acetic acid is similar to the absorbance of the control (untreated) Cellulose, showing that acetic acid has not effectively modified the physical structure of the Cellulose.

Absorption Test

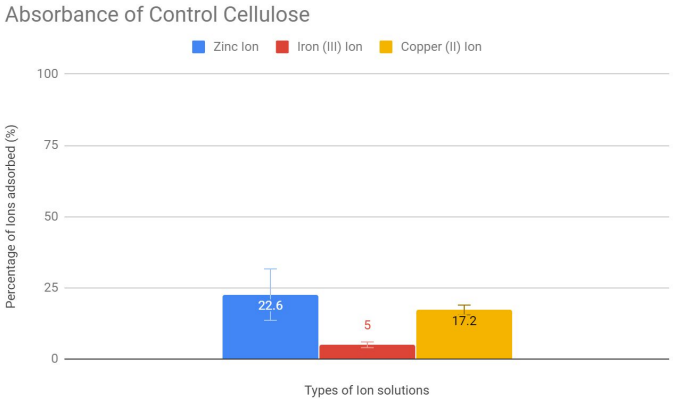

Figure 14: Bar Graph for absorbance of control Cellulose

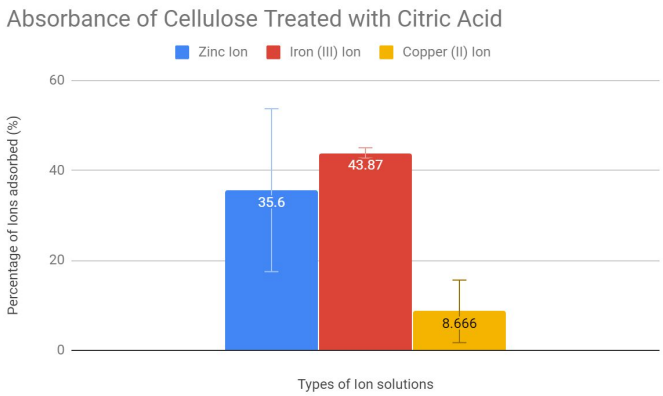

Figure 15: Bar Graph for absorbance of Cellulose treated with citric acid

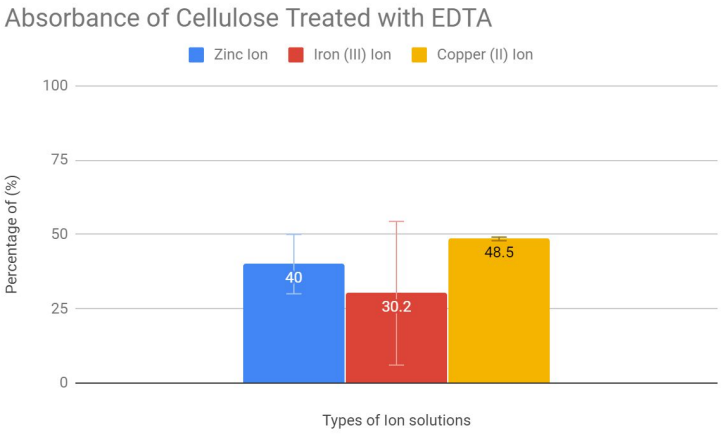

Figure 16: Bar Graph for absorbance of Cellulose treated with EDTA

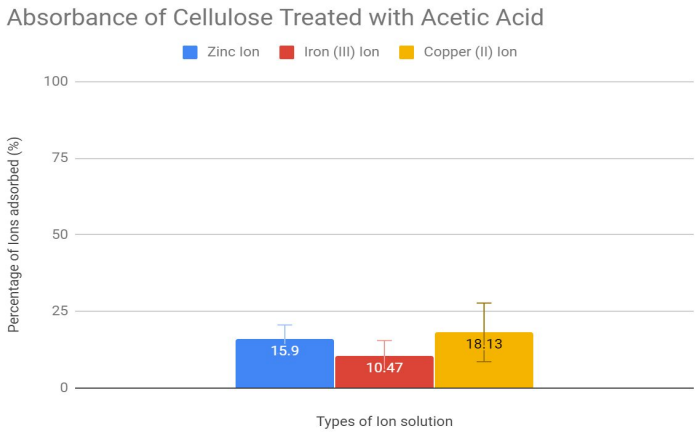

Figure 17: Bar Graph for absorbance of Cellulose treated with acetic acid

In Figure 14, the ion adsorbed most by the control Cellulose was the Zinc ions (22.6%), whereas ion adsorbed least by the control Cellulose was the Iron (III) ions (5%).

In Figure 15, the ion adsorbed most by the Cellulose treated with citric was Iron (III) ion (43.9%), whereas the ion adsorbed least by the Cellulose treated with citric acid was Copper ions (8.67%).

In Figure 16, the ion adsorbed most by the Cellulose treated with EDTA was the Copper (II) ions (48.5%), whilst the ion adsorbed least by the Cellulose treated with EDTA was the Iron (III) ion (30.2%). EDTA is a chelating agent, hence it will chelate around the metal ions, hence adsorbing them.

In Figure 17, the ion adsorbed most by the Cellulose treated with acetic acid was the Copper (II) ions (18.13%) whereas the ion absorbed least by the Cellulose treated with acetic acid was the Iron (III) ions (10.47%).

The treated Cellulose generally have a much better metal ion adsorption. The adsorption of metal ions could be due to the interaction between the metal ions and the carboxylate ions in the treated cellulose through dative bonding.

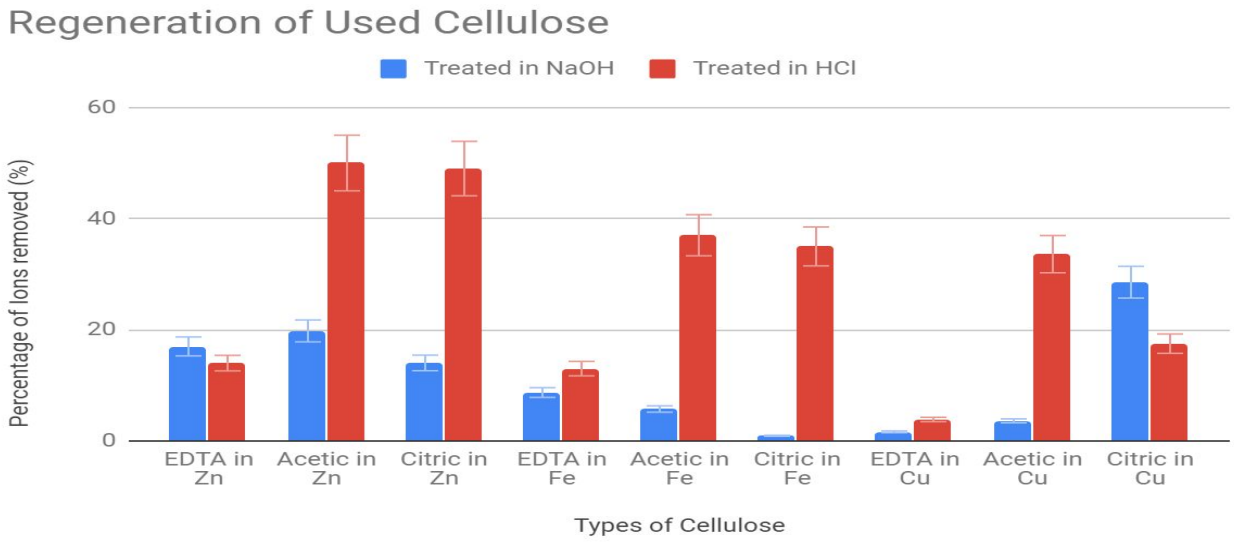

Figure 18: Bar graph for the regeneration of Used Cellulose

In Figure 18, the largest percentage of regeneration is found in Cellulose treated with acetic acid which had adsorbed zinc ions, whereas the lowest percentage of regeneration is found in cellulose treated in citric acid which had adsorbed Iron (III) ions. Hydrochloric (HCl) acid has also adsorbed more metal ions as compared to Sodium Hydroxide (NaOH) in general. This may be because that Hydrochloric Acid is able to protonate the carboxylate ions (COO^-) in EDTA and citric acid to form carboxylic acid group (COOH), hence preventing it from interacting with metal ions. Thus, hydrochloric acid is more effective in regenerating the adsorbent.

Conclusion

The Cellulose treated with citric acid was found to have the highest adsorption for Copper (II) ions, Zinc ions and Iron (III) ions. The Cellulose treated with acetic acid has similar adsorption of all 3 heavy metal ions to that of the cellulose in the control set-up. Future experiments could be done to identify if other heavy metal ions could be adsorbed as efficiently as shown in the experiments above using citric acid and the procedure of adsorption and bleaching can be repeated a number of times to see if there is a decrease in the percentage adsorption of metal ions. Also, the ratio of acid to Cellulose in the regeneration process could be increased further to find out if the Cellulose could be bleached more effectively and could be bleached of more heavy metal ions.

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