Adsorption of heavy metal ions and dyes and synthesis of bioethanol using honeydew peels and watermelon piths

Atticus Phang (2i201)

Isaac Kok (2i209)

Lai Jun Yu (2i215)

Sia Zhi Hung (2i224)

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Abstract

This project investigated the multi-purpose usage - adsorption of heavy metal ions and dyes, and synthesis of biofuels - of dried fruit wastes: watermelon piths and honeydew peels. The experiment involved pretreating the dried waste with acid, then allowed to ferment with Zymomonas mobilis to produce bioethanol. The dried waste was also investigated on its properties in removing heavy metal ions (copper(II) and zinc ions) and dyes (Methylene blue, Malachite green, Brilliant green, Direct red, Methyl orange). In conclusion, bioethanol was successfully synthesized, watermelon piths was significantly better in the adsorption of heavy metal ions, and anionic dye Direct red and cationic dye Methylene blue, and honeydew peels were significantly better in the adsorption of cationic dyes Malachite and Brilliant green, and no significant difference in the adsorption of Methyl orange.

1. Introduction

1.1. Rationale

Removal of heavy metal ions from wastewater is essential because of their extreme environmental, public health and economic impacts (Fakhre and Ibrahim, 2018).

Dye removal from textile effluents is a major environmental problem because of the difficulty to treat such streams (Annadurai, Juang and Lee, 2002).

The rising cost and dwindling supply of oil have been focusing attention on possible routes to making chemicals, fuels, and solvents from biomass instead. (Tuck et al, 2012).

1.2. Literature Review

Heavy metals are elements having atomic masses between 63.5 and 200.6, and a specific gravity greater than 5.0 (Srivastava and Majumder, 2008). With the rapid development of industries such as metal plating facilities, wastewaters contaminated by heavy metal ions are directly or indirectly discharged into the environment increasingly, especially in developing countries. Unlike organic contaminants, heavy metals are non-biodegradable and tend to accumulate in living organisms with many of such heavy metal ions known to be toxic or carcinogenic. (Fu, F., & Wang, Q., 2011). Most of the adsorption studies have been focused on untreated plant wastes such as papaya wood (Saeed et al., 2005), maize leaf (Babarinde et al., 2006), teak leaf powder (King et al., 2006), lalang (Imperata cylindrica) leaf powder (Hanafiah et al., 2007), rubber (Hevea brasiliensis) leaf powder (Hanafiah et al., 2006b,c), Coriandrum sativum (Karunasagar et al., 2005), peanut hull pellets (Johnson et al., 2002), etc. However, little or none of the research has been done on fruit wastes such as honeydew peels or watermelon piths.

Dyes are harmful to aquatic life in rivers where they are discharged. The occupational exposure of workers in the textile industries is linked to a higher bladder cancer risk. The use of hair colouring products and breast cancer have also been linked. Various agricultural products and by-products have been investigated to remove dyes from aqueous solutions. These include cotton waste, rice husk, bark (Gupta, G., Prasad, G., Panday, K., & Singh, V., 1988), sugar industry mud (Magdy, Y., & Daifullah, A., 1998), palm-fruit bunch(Nassar, M. M., Hamoda, M. F., & Radwan, G. H., 1995), Jackfruit peel (Inbaraj BS, Sulochana N., 2002), wood (Ho YS, McKay G., 1998), orange peel (Namasivayam C, Muniasamy N, Gayatri K, Rani M, Ranganathan K., 1996), etc.. The distinct advantage of this method is the lower costs involved. Hence, there is a need to search for more economical and effective sorbents. (Ho, Y.-S., Chiang, T.-H., & Hsueh, Y.-M., 2005).

Our strong dependence on fossil fuels comes from the intensive use and consumption of petroleum derivatives which, combined with diminishing petroleum resources, causes environmental and political concerns. There is clear scientific evidence that emissions of greenhouse gases (GHG), such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), arising from fossil fuel combustion and land-use change as a result of human activities are perturbing the Earth's climate (IPCC, 2017). Concerning chemicals, their dependence on fossil resources is even stronger. The majority of chemical products are produced from oil refinery and almost 4% of oil is worldwide used for chemical and plastic production (Nossin PMM, 2009). Biomass is emerging as a possible renewable alternative to petroleum-based resources in light of increasing environmental, economic, and political difficulties associated with fossil fuel extraction and use (Luterbacher, J. S., Rand, J. M., Alonso, D. M., Han, J., Youngquist, J. T., Maravelias, C. T., … Dumesic, J. A., 2014).

Hence, the aim of this study is to research on the multi-purpose usage of waste materials, specifically watermelon piths and honeydew peels in the adsorption of heavy metal ions, dyes, and the synthesis of bioethanol.

2. Objectives and hypotheses

2.1. Objectives

2.1.1. To investigate and compare the effectiveness of cellulose waste derived from watermelon piths and honeydew peels in the adsorption of Copper(II) ions and Zinc ions.

2.1.2. To investigate and compare the effectiveness of cellulose waste derived from watermelon piths and honeydew peels in the adsorption of Malachite green, Direct red, Methylene blue, Brilliant green and Methyl orange.

2.1.3. To investigate and compare the effectiveness of the adsorption of dyes in dye solutions of varying pH.

2.1.4. To synthesize bioethanol from watermelon piths and honeydew peels.

2.2. Hypothesis

2.2.1. There will be at least 70% adsorption of the Copper(II) ions, Zinc ions, Malachite green, Direct red, Methylene blue, Brilliant green, and Methyl orange regardless of waste used.

2.2.2. Cellulose waste extracted from honeydew peels is more effective in the adsorption of Copper(II) ions, Zinc ions, Malachite green, Direct red, Methylene blue and Brilliant green than watermelon piths.

2.2.3. Changes in pH will have minimal effect on the adsorption of dyes.

2.2.4. Biofuels can be synthesized from watermelon pith and/or honeydew peels

3. Methods and Materials

3.1. Materials

3.1.1.

Honeydew peels	Watermelon Piths
Copper(II) sulfate	Zinc sulfate
Malachite green	Brilliant green
Direct red	Methylene blue
Methyl orange	1% Sulfuric acid
Zymomonas mobilis	Deionized water
Hydrochloric Acid	Sodium Hydroxide

3.2. Apparatus

3.2.1.

DR/890 Colorimeter	UV-VIS spectrophotometer
Autoclave	Centrifuge
Ethanol meter	Weighing scale
Orbital shaker	Incubator
Spirit burner	Oven
Blender	pH meter

3.3. Methods

3.3.1. Experiment 1: Extraction of hemicellulose

Honeydew peels and watermelon pith are pretreated with 1% sulfuric acid in an autoclave reactor for 121°C for 1 hour. The liquid phase (hemicellulose hydrolysate) is obtained through filtration. (Zhou, et al., 2018)

3.3.2. Experiment 2: Synthesis of bioethanol

Zymomonas mobilis is cultivated with broth before being left to incubate for 3 days. Afterwhich, the broth is centrifuged at 10°C at 5000 rpm for 10 minutes to extract Zymomonas mobilis. Zymomonas mobilis is added to the hemicellulose hydrolysate solution, which is left to ferment for 3 days at 30°C. Afterwhich, an Ethanol meter is used to measure the concentration of ethanol produced.

3.3.3. Experiment 3: Adsorption of copper(II) and zinc ions

5 replicates of 0.5g of the dried fruit waste is submerged into 20ml of 25ppm of each respective heavy metal ion solution and shaken at 200 rpm for 4 hours. Afterwhich, the solution was centrifuged to obtain the liquid, which the concentration of heavy metal ions remaining in the solution was measured using the DR/890 colorimeter.

3.3.4. Experiment 4: Adsorption of dyes

5 replicates of 0.5g of the dried fruit waste is submerged into 20ml of 25ppm of each respective dye solution and shaken at 200 rpm for 4 hours. Afterwhich, the solution was centrifuged to obtain the liquid, which the concentration of the dye remaining in the solution was measured using the UV-VIS spectrophotometer.

3.3.5. Experiment 5: Adsorption of dyes using pH control

3 replicates of 0.5g of the dried fruit waste is submerged into 20ml of 25ppm of each respective dye solution varying from pH4, pH6, pH8, and pH10 and shaken at 200 rpm for 4 hours. Afterwhich, the solution was centrifuged to obtain the liquid, which the concentration of the dye remaining in the solution was measured using the UV-VIS spectrophotometer.

4. Results and Discussion

4.1. Characterization

4.1.1. Fourier-transform infrared spectroscopy (FTIR)

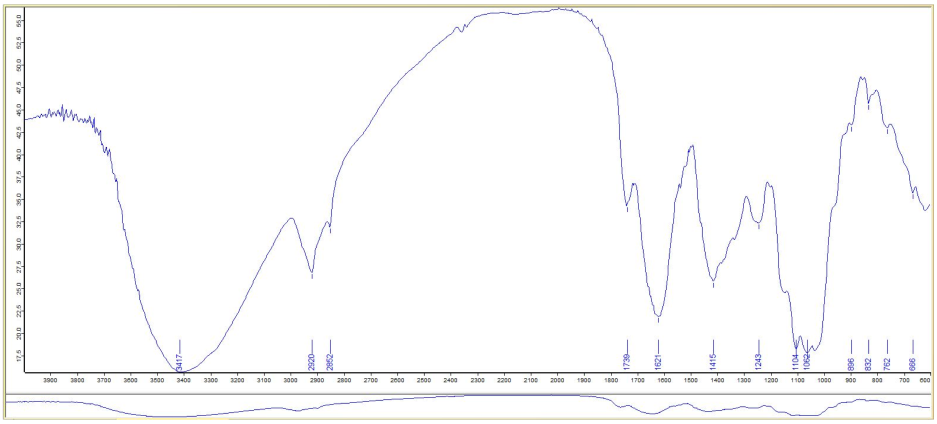

Figure 1: FTIR spectrum for powdered Honeydew peels

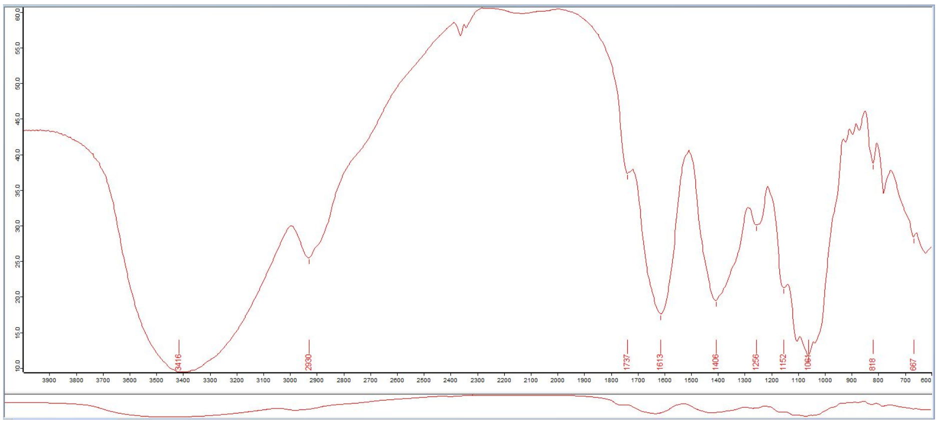

Figure 2: FTIR spectrum for powdered Watermelon piths

Both FTIR spectrum shows a peak at 3416 and 3417 cm^{-1}, indicating the presence of O-H stretch. This hydroxyl group is crucial as they have lone pairs that can act as ligands and can form dative bonds with heavy metal ions

4.1.2. Scanning Electron Microscope (SEM)

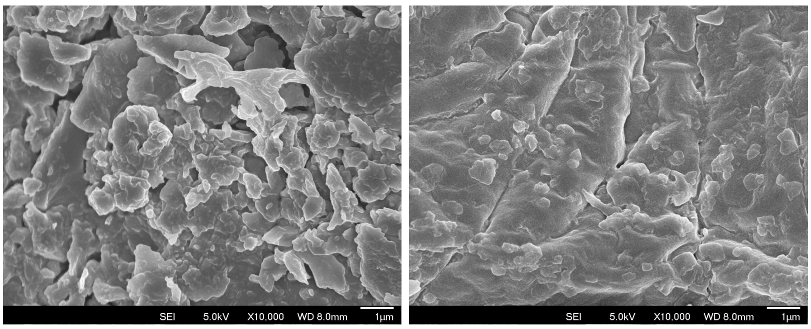

Figure 3 & 4: SEM image of powdered honeydew peels and watermelon piths respectively at 10,000 magnification

The surface morphology of the powdered peels shows high surface area which is used as active sites for adsorption.

4.2. Bioethanol production

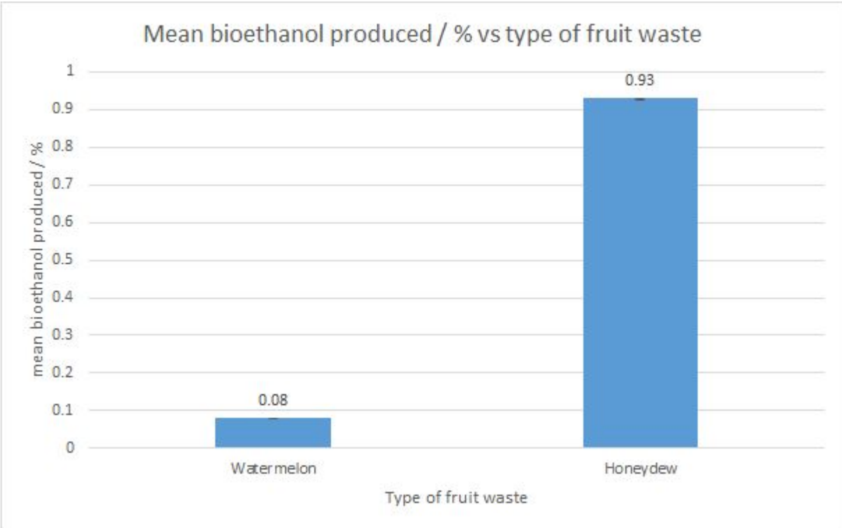

Figure 7: Mean bioethanol produced / % vs type of fruit waste

Using honeydew peels and watermelon piths, bioethanol was successfully synthesized. Honeydew peels also synthesized 12.4 times more bioethanol than watermelon piths.

4.3. Adsorption of copper(II) and zinc ions

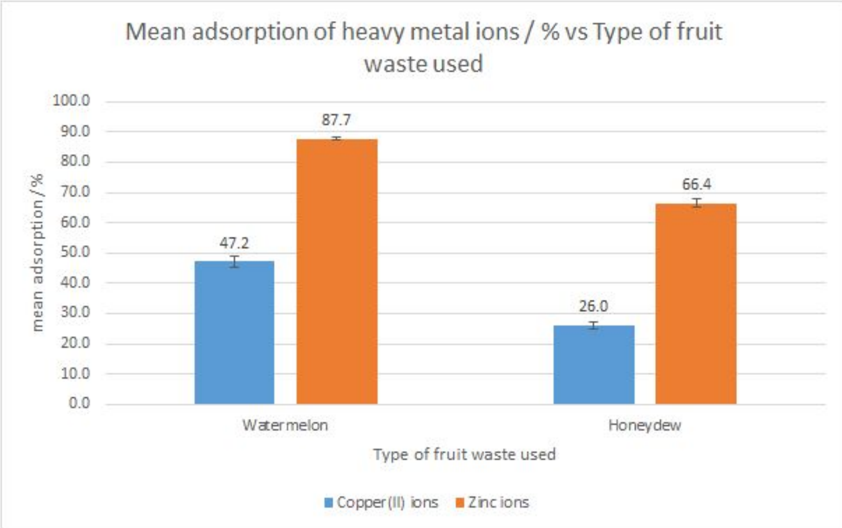

Figure 8: Mean adsorption of heavy metal ions / % vs type of fruit waste

For the adsorption of both copper(II) ions and zinc ions, watermelon pith performed 21.20% better for copper(II) ions and 21.28% better for zinc ions compared to honeydew peels.

4.3.1. Mann-Whitney U-Test

Sample Comparison	p-value	Conclusion
Watermelon pith against Honeydew peels for the adsorption of copper(II) ions	0.012 (<0.05)	Significant difference
Watermelon pith against Honeydew peels for the adsorption of zinc ions	0.012(<0.05)	Significant difference

Hence, watermelon piths are significantly better at the adsorption of copper(II) and zinc ions than honeydew peels.

4.4. Adsorption of dyes

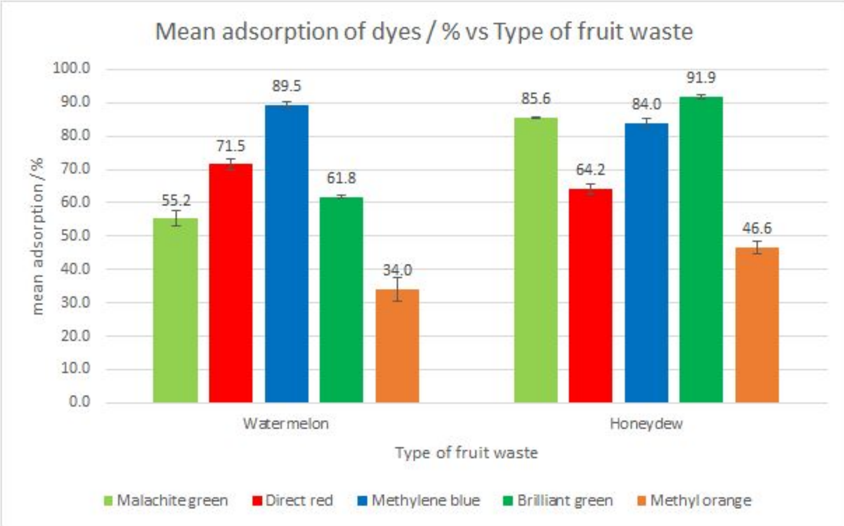

Figure 9: Mean adsorption of dyes / % vs type of fruit waste

For Malachite green and Brilliant green (cationic dyes), honeydew peels performed 30.3% and 30.1% respectively better than watermelon piths, and recorded at least 85% adsorption, while watermelon piths only recorded at least 55% adsorption.

For Direct red (anionic) and Methylene blue (cationic), watermelon piths performed 7.28% and 5.5% respectively better than honeydew peels, and recorded at least 70% adsorption, while honeydew peels only recorded at least 60% adsorption.

For Methyl orange (anionic), honeydew peels performed 12.6% better than watermelon piths. However, none of them manage to achieve 50% adsorption.

4.4.1. Mann-Whitney U-Test

Sample Comparison	p-value	Conclusion
Watermelon pith against Honeydew peels for the adsorption of Malachite green	0.012 (<0.05)	Significant difference
Watermelon pith against Honeydew peels for the adsorption of Direct red	0.037(<0.05)	Significant difference
Watermelon pith against Honeydew peels for the adsorption of Methylene blue	0.012(<0.05)	Significant difference
Watermelon pith against Honeydew peels for the	0.012(<0.05)	Significant difference

adsorption of Brilliant green		
Watermelon pith against Honeydew peels for the adsorption of Methyl orange	0.059(>0.05)	No Significant difference

Hence, watermelon piths are significantly better at the adsorption of Direct red and Methylene blue, while honeydew peels are significantly better at the adsorption of Brilliant green and Malachite green. For the adsorption of Methyl orange, there is no significant difference between watermelon piths and honeydew peels.

4.5. Adsorption of dyes using pH control

4.5.1. Direct red

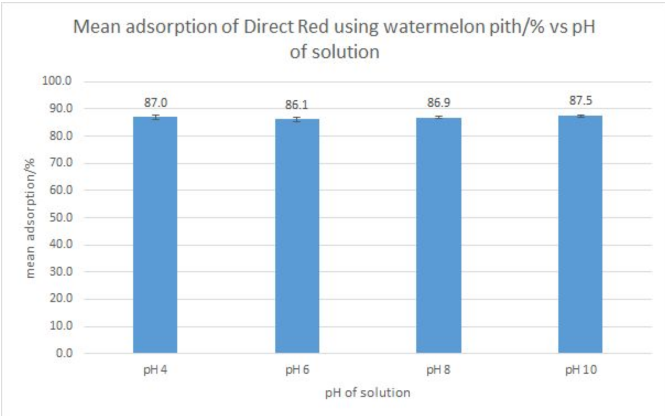

Figure 10: Mean adsorption of Direct red using watermelon pith / % vs pH of solution

Between all the pH levels, the average adsorption is 86.9%. There is not much difference between the results gathered the respective pH(s). The standard deviation for the set of data represented in Figure 4 is 0.57.

4.5.2. Methylene blue

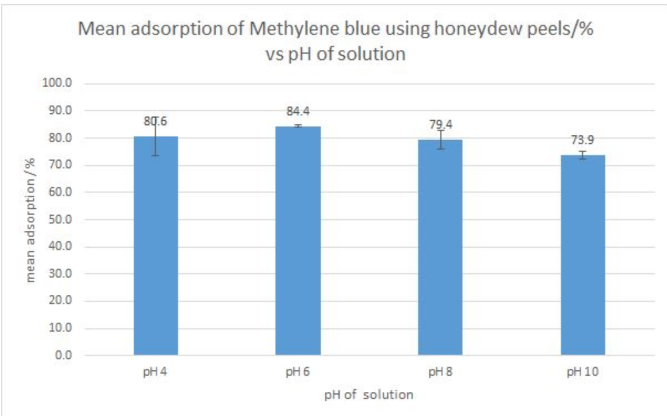

Figure 11: Mean adsorption of Methylene blue using honeydew peels / % vs pH of solution

At pH 6, the mean adsorption was recorded at 84.4% while at pH10, the mean adsorption was recorded at 73.9%. The standard deviation of the set of data represented in Figure 5 is 4.34.

5. Conclusion and Recommendations for future work

5.1. Adsorption of heavy metal ions

Watermelon piths are significantly better at the adsorption of both copper(II) and zinc ions compared to honeydew peels.

5.2. Adsorption of dyes

Watermelon piths are significantly better at the adsorption of Direct red and Methylene blue compared to honeydew peels.

Honeydew peels are significantly better at the adsorption of Brilliant green and Malachite green compared to watermelon piths.

For the adsorption of Methyl orange, there is no significant difference between watermelon piths and honeydew peels.

5.3. Adsorption of dyes in varying pH solution

There is no noticeable difference with regards to the adsorption of Direct red in solutions pH varying at 4, 6, 8, and 10.

For the adsorption of Methylene blue in solutions pH varying at 4, 6, 8, and 10, the best and worst adsorption are recorded at pH 6 and pH 10 respectively.

5.4. Bioethanol

Bioethanol was successfully synthesized from both watermelon piths and honeydew peels.

5.5. Recommendations for future work

More optimization can be completed to find the best conditions in which there will be maximum adsorption. In addition, the dye adsorption in varying pH solutions can be extended to include other dyes and heavy metal ions, and tested with 5 replicates so further statistical analysis can be done. Furthermore, instead of bioethanol, the dried fruit waste can be investigated if they can be synthesized to form biofuels.

6. References

Al-Senani, G. M., & Al-Fawzan, F. F. (2018). Adsorption study of heavy metal ions from aqueous solution by nanoparticle of wild herbs. The Egyptian Journal of Aquatic Research,44(3), 187-194.

Annadurai, G., Juang, R., & Lee, D. (2002). Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. Journal of Hazardous Materials, 92(3), 263-274.

Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: A review. Journal of Hazardous Materials, 157(2-3), 220-229.

Fakhre, N. A., & Ibrahim, B. M. (2018). The use of new chemically modified cellulose for heavy metal ion adsorption. Journal of Hazardous Materials,343, 324-331.

Karmee, S. K. (2016). Liquid biofuels from food waste: Current trends, prospect and limitation. Renewable and Sustainable Energy Reviews,53, 945-953.

Liu, & Peng. (2016, September 30). Adsorption behavior of heavy metal ions from aqueous medium on nanocellulose. Retrieved from http://www.diva-portal.org/smash/record.jsf?pid=diva2:999523&dswid=1481

Ngah, W. W., & Hanafiah, M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. Bioresource Technology, 99(10), 3935-3948.

Reddy, N., & Yang, Y. (2009). Extraction and characterization of natural cellulose fibers from common milkweed stems. Polymer Engineering & Science, 49(11), 2212-2217.

Tang, L., Huang, B., Ou, W., Chen, X., & Chen, Y. (2011). Manufacture of cellulose nanocrystals by cation exchange resin-catalyzed hydrolysis of cellulose. Bioresource Technology, 102(23), 10973-10977.

Tuck, C. O., Perez, E., Horvath, I. T., Sheldon, R. A., & Poliakoff, M. (2012). Valorization of Biomass: Deriving More Value from Waste. Science, 337(6095), 695-699. doi:10.1126/science.1218930

Ververis, C., Georghiou, K., Danielidis, D., Hatzinikolaou, D., Santas, P., Santas, R., & Corleti, V. (2007). Cellulose, hemicelluloses, lignin and ash content of some organic materials and their suitability for use as paper pulp supplements. Bioresource Technology, 98(2), 296-301.

Wang, Q. Q., Zhu, J. Y., Reiner, R. S., Verrill, S. P., Baxa, U., & Mcneil, S. E. (2012). Approaching zero cellulose loss in cellulose nanocrystal (CNC) production: Recovery and characterization of cellulosic solid residues (CSR) and CNC. Cellulose, 19(6), 2033-2047.

Yu, X., Tong, S., Ge, M., Wu, L., Zuo, J., Cao, C., & Song, W. (2013). Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals. Journal of Environmental Sciences, 25(5), 933-943.

Zhou, H., Zhan, W., Wang, L., Guo, L., & Liu, Y. (2018). Making Sustainable Biofuels and Sunscreen from Corncobs To Introduce Students to Integrated

Biorefinery Concepts and Techniques. Journal of Chemical Education, 95(8), 1376-1380.