Investigating effectiveness of pyrolysis and magnetisation of coffee grounds on adsorption of different heavy metal ions and dyes

Li Jun Liang (3S3), Bennett Ho (3S3) and Chin Cherng Yuen (3S2)

Group 1-45

Abstract

Heavy metal ions and dyes are abundant in discharged waters from sources of petrol and industrial effluents, leaching from soil etc. This has proved to be a pressing issue as it poses a threat to the environment and this is coupled with the fact that dyes are highly toxic in nature. Conventional methods of using activated carbon to purify wastewater is extremely costly. Since spent coffee grounds is a porous carbon material suited to adsorb heavy metal ions and dyes, this study aims to investigate the effectiveness of pyrolysis and magnetisation of coffee grounds to improve on the adsorption of Cu^{2+} ions and dyes by spent coffee grounds for water purification. The study involves using *Coffea Arabica* from Mccafe as the adsorbent to compare the effectiveness of pyrolysis in enhancing the adsorption capabilities of spent coffee grounds. Furthermore, we magnetised a portion of the unpyrolysed coffee grounds to compare to the unpyrolysed coffee grounds to investigate the effects of magnetisation on the adsorption capabilities of spent coffee grounds. In the experiment, 1g of spent coffee grounds were added into 20ml of the pollutant solution and put on the orbital shaker for 3h to shake. Subsequently, the sample was centrifuged and the pollutant solution was extracted. The pollutant solutions were then tested to determine the effects of pyrolysis and magnetisation on the adsorption of Cu^{2+} ions and dyes by the use of a colorimeter and UV-vis spectrophotometer respectively to find out the concentration of the pollutant solution remaining. The percentage adsorption of pollutants was calculated. According to the results, pyrolysed spent coffee grounds when compared to unpyrolysed coffee grounds has seen significantly greater adsorption capabilities of coffee grounds to adsorb Cu^{2+} ions and all dyes while magnetisation of unpyrolysed coffee grounds, when compared to unmagnetised unpyrolysed coffee grounds only significantly increased the adsorption of Cu^{2+} ions, direct red and methyl orange dyes. Thus, this project opens many new doors and cost effective methods of utilising both pyrolysis and magnetisation on spent coffee grounds for adsorption of heavy metal ions and dyes in polluted wastewater.

Introduction

Recently, there has been increased research in the field of coffee biomass-derived carbon porous materials, both due to its unique physiochemical properties and cost effectiveness (Veerakumar *et al.,* 2016) , as well as its potential to allow safe disposal of coffee grounds, which pose a threat due to high oxygen demand during decomposition and potential release of residual caffeine, tannin, and polyphenol contaminants to the environment. Metal-binding polyhydroxy polyphenol functional groups and present in large quantities in instant coffee. (Utomo & Hunter, 2006). According to Veerakumar *et al.* (2016), activated carbon, which is similar to biochar, has high surface areas and enriched surface functionalities. Furthermore, biochar has high porosity, high specific surface area, and a cation exchange capacity. (Komkiene & Baltrenaite, 2015) These properties are of interest as the polyhydroxy polyphenol functional groups provide efficient absorption of heavy metal ions over a fairly wide pH range (Otomo & Hunter, 2006).Other research also point out that magnetisation of biochar is useful for easy extraction using magnets to remove magnetised adsorbents from water. Also, the high porosity and surface area of biochar serves as a promising alternative as an adsorbent material that can be efficiently used in purifying, discoloring, recuperating and removing odors from metal polluted water treatment. (Agrawal, Vairagade & Kedar, 2017). Furthermore, coffee is one of the largest agricultural commodities traded worldwide, with annual production of coffee grounds at ∼8 billion kg per year. Commercial coffee beverage production generates substantial quantities of spent grounds that present a significant waste disposal challenge. This is due to the coffee grounds' high oxygen demand during decomposition and potential release of residual caffeine, tannin, and polyphenol contaminants to the environment. (Silva et al., 1998). Thus, an alternative solution to dispose used coffee grounds is needed to prevent damage to the environment. In addition, there has been much interest recently in new and sustainable solutions to remove heavy metals from contaminated water and soil. Unreasonable mining and smelting of mineral resources, solid waste disposal, sewage irrigation, utilization of pesticides and fertilizers has resulted in a large number of heavy metal pollutants into the water and soil environment, causing serious damage to public health and ecological safety. (Wang et al., 2018). On the other hand, there has also been increased interest in new and sustainable methods to remove dues from contaminated wastewater as materials are discharged into the environment every year (Pirkarami & Olya, 2017) and the dyeing materials are highly toxic in nature as it contains high suspended solid, COD, dye and chemicals (Noel & Rajan, 2014)

Hence, this study aims to utilise spent coffee grounds as a cost effective adsorbent as means for water purification. Also, this study aims to study the effects of pyrolysis and investigate its effectiveness for the adsorption of heavy metal ions and dyes in wastewater. Lastly, this study aims to study the effects of magnetisation on the effectiveness for adsorption of heavy metal ions and dyes in wastewater.

Objectives

This study aims to:

1. To investigate the effectiveness of unpyrolysed and pyrolysed coffee grounds in the removal of Cu^{2+} ions and dyes.
2. To investigate how magnetisation will affect the effectiveness of the coffee grounds the removal

of Cu^{2+} ions and dyes.

Hypothesis

1. Pyrolysed coffee grounds would be more effective in removing Cu^{2+} ions and dyes compared to unpyrolysed grounds.
2. Magnetisation of the coffee grounds would inhibit the effectiveness of coffee grounds in removing Cu^{2+} ions and dyes slightly.

Materials and Methods

Materials

Hydrated Iron(II) Chloride, 25% aqueous ammonia, copper(II) sulfate ($CuSO_4$), iron(III) nitrate, methylene blue dye, brilliant green dye, direct red dye and methyl orange dye were obtained from the Hwa Chong Institution Chemistry Lab. Spent *Coffea Arabica* grounds were obtained from Mccafe.

Preparation of Unpyrolysed Coffee Grounds

Coffea Arabica spent coffee grounds were obtained from McCafe and were subsequently washed and dried with DI water in a sieve for approximately 20min until the filtrate was clear. After that, they were put onto a tray and left to dry overnight in the oven at 70°C. Finally, the spent coffee grounds we collected and stored in a vial.

Synthesis of Pyrolysed Coffee Grounds

Coffea Arabica spent coffee grounds were obtained from McCafe and were subsequently washed and dried with DI water in a sieve for approximately 20min until the filtrate was clear. After that, they were put onto a tray and left to dry overnight in the oven at 70°C. The spent coffee grounds were then collected and placed in an ashing furnace at 600°C for 40min. Finally, after being left to cool back to room temperature, the spent coffee grounds were collected and stored in a plastic vial.

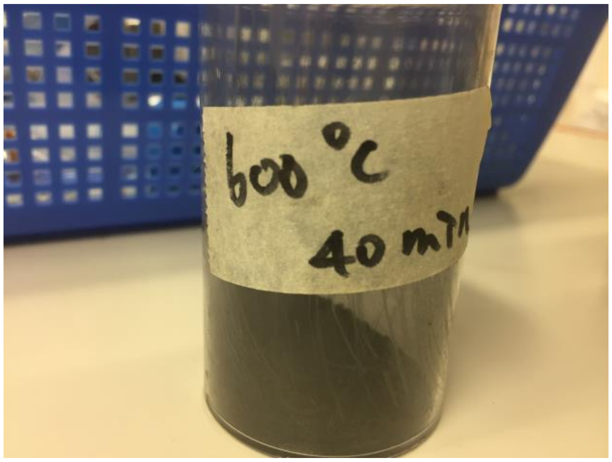

Figure 1: Pyrolysed coffee grounds collected from ashing furnace

Synthesis of Magnetised Coffee Grounds

Coffea Arabica spent coffee grounds were obtained from McCafe and subsequently washed and dried with DI water in a sieve for approximately 20min. Subsequently, 6.66g of $FeCl_2$ was added into 13.39g hydrated $Fe_3(SO_4)_2$ and was dissolved into 45ml of DI water. 5g of unpyrolysed coffee grounds were added into the mixture for stirring with use of a hot plate and a magnetic stirrer for 10min. In the fume hood, 25ml of 25% aqueous ammonia was added into the mixture in order to coat the coffee grounds with pure magnetite. Each solution was stirred thoroughly for 1min and left to settle for 45min. Each sample was them filtered using vacuum filtration by the use of a Buchner funnel and washed adequately with DI water until pH neutral of 7 was achieved. It was then transferred to a petri dish to be left to dry at 70 °C overnight in the oven. Finally, upon being dried, it was collected and stored in a plastic vial.

Synthesis of Pure Magnetite

6.66g of $FeCl_2$ was added into 13.39g hydrated $Fe_3(SO_4)_2$ and was dissolved into 45ml of DI water. Subsequently, it was stirred using a magnetic stirrer on a hot plate for 10min. In the fume hood, 25ml of 25% aqueous ammonia was added into the mixture in order to produce pure magnetite. Each solution was stirred thoroughly for 1min and left to settle for 45min. Each sample was them filtered using vacuum filtration by the use of a Buchner funnel and washed adequately with DI water until a neutral pH of 7 was achieved. It was then transferred to a petri dish to be left to dry at 70°C overnight in the oven. Finally, upon being dried, it was collected and stored in a plastic vial.

Experiment for Testing of adsorption of Cu^{2+} ions and Dyes

1.0g of spent coffee grounds was put into a centrifuge tube filled with 20ml of the various heavy metal ion/dye solution, which includes CuSO4 solution (50ppm of Cu^{2+} ions), Methylene Blue solution (50ppm), Brilliant Green solution (50ppm), Direct Red solution (50ppm), and Methyl Orange solution (50ppm). The suspension was then put onto the orbital shaker at 250rpm for 3h before collection. Centrifugation of the samples for 10min at 10000rpm was done to separate the unmagnetised coffee grounds from the respective pollutant solution while the magnetised spent coffee grounds were removed from the respective pollutant solutions by use of a magnet. The dye/Cu^{2+} ion solution was extracted and diluted in a volumetric flask by 10 times. 5 replicates were done for each respective pollutant solution and type of spent coffee grounds, with the controls being the respective pollutant solution without addition of any spent coffee grounds. The results of the adsorption of methylene blue solution, brilliant green solution, direct red solution, and methyl orange solution were obtained via the use of a UV spectrometer at wavelengths 664.0nm, 624.0nm, 528.0nm and 464.0nm respectively. The percentage adsorption was calculated via use of respective calibration curves. On the other hand, the Cu^{2+} ion test was done by the use of a colorimeter where the colour reagent of Cu^{2+} ion was added to the diluted Cu^{2+} ion solution from the volumetric flask. Finally, the percentage adsorption of the various pollutants were calculated and recorded down.

Results and Discussion

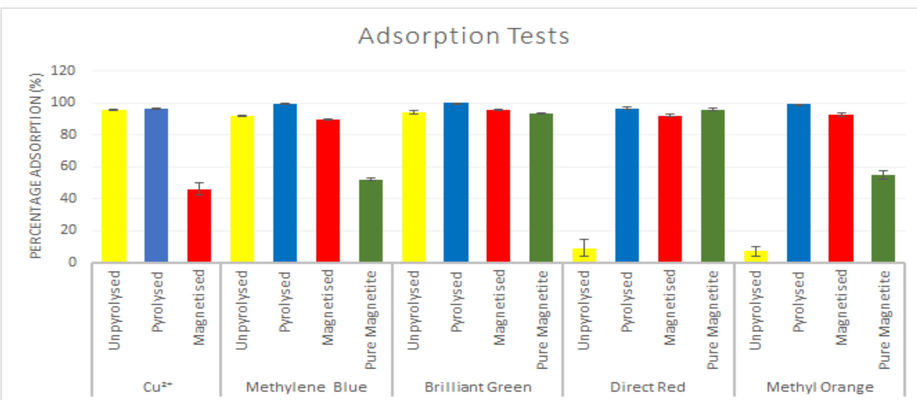

Figure 2: Percentage adsorption of each dye

Cu^{2+} ion adsorption percentage of various coffee grounds

From the Cu^{2+} ion percentage adsorption bar chart, it can be concluded that pyrolysis of coffee grounds does not significantly improve the adsorption capability of spent coffee grounds (p-value = 0.830 > 0.05). However, magnetisation of coffee grounds significantly decreases the ability of the spent coffee grounds to be able to adsorb Cu^{2+} ions (p-value = 0.012 < 0.05).

Percentage of methylene blue adsorption by various coffee grounds

From the methylene blue adsorption bar chart, it can be concluded that pyrolysis of coffee grounds significantly increase the adsorption capabilities of spent coffee grounds. Also, magnetisation of coffee grounds will significantly decrease the ability for the coffee grounds to be able to adsorb methylene blue dye.

Percentage of brilliant green adsorption by various coffee grounds

From the brilliant green adsorption bar chart, it can be concluded that pyrolysis of coffee grounds has resulted in a significant increase in capability for spent coffee grounds to be able to adsorb brilliant green dyes. On the other hand, magnetisation results in an insignificant increase in ability to adsorb brilliant green dye.

Percentage of direct red adsorption by various coffee grounds

From the direct red adsorption bar graph as shown above , there is a significant increase of direct red dye adsorption capability when spent coffee grounds are pyrolysed. Also, it can be concluded that magnetisation also significantly increases ability for the spent coffee grounds to adsorb direct red dyes.

Percentage of methyl orange adsorption by various coffee grounds

From the methyl orange adsorption chart as shown above (Figure 7), it can be concluded that pyrolysis significantly increases the capability for spent coffee grounds to adsorb methyl orange dyes. Also, magnetisation significantly increases the capability for spent coffee grounds to adsorb methyl orange dye as well.

Therefore, as seen from the Cu^{2+} ion test, methylene blue test, brilliant green test, direct red test, and the methyl orange test, and from their respective bar graphs, pyrolysis significantly improves the ability of the coffee grounds to adsorb both cationic (methylene blue dye and brilliant green dye) and anionic (direct red dye and methyl orange dye) dyes but not Cu^{2+} ions. However, while magnetisation significantly improves the adsorption capability of coffee grounds to adsorb anionic dyes (direct red dye and methyl orange dye), it does not significantly affect the ability of coffee grounds to adsorb cationic dyes (methylene blue dye and brilliant green dye) and Cu^{2+} ions.

Mann Whitney U-test

Type of dye/heavy metal solution	Unpyrolysed and Pyrolysed Coffee	P-value	Unpyrolysed and Magnetised	P-value

	Grounds		Coffee Grounds	
Cu^{2+}	Not significant	0.830	Significantly decreases adsorption capabilities	0.012
Methylene Blue solution	Significantly increases adsorption capabilities	0.011	Significantly decreases adsorption capabilities	0.012
Brilliant Green solution	Significantly increases adsorption capabilities	0.012	Not significant	0.144
Direct Red solution	Significantly increases adsorption capabilities	0.012	Significantly increases adsorption capabilities	0.012
Methyl Orange solution	Significantly increases adsorption capabilities	0.012	Significantly increases adsorption capabilities	0.012

FTIR Tests

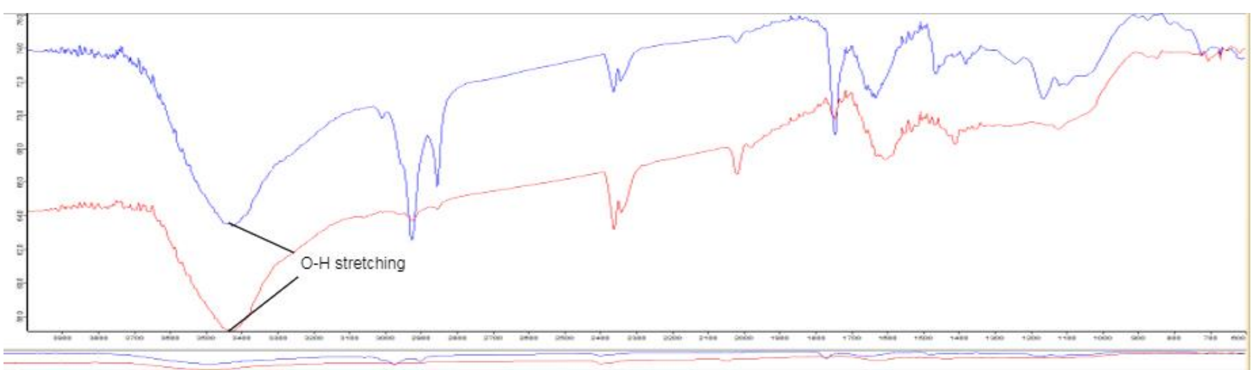

Figure 3: FTIR Results for unpyrolysed coffee grounds and pyrolysed coffee grounds

FTIR tests were conducted on samples of pyrolysed coffee grounds, unpyrolysed coffee grounds, and magnetised coffee grounds. From the results obtained from the FTIR scan, it can be found that there is presence of O-H stretching of hydroxyl groups in both pyrolysed and unpyrolysed coffee grounds.

Conclusion

Coffee grounds proved to be able to adsorb Cu^{2+} ions and dyes, as the hydroxyl groups found in both pyrolysed and unpyrolysed enables the adsorption of Cu^{2+} ions as the oxygen atom in the O-H bond contains a lone pairs of electrons that can be readily accepted by Cu^{2+} ions to form dative bonds. Also, it enhances adsorption of dyes by forming permanent dipole-permanent dipole interactions with dye molecules near their dipoles, and the lone pair of electrons on the oxygen atom also allows it to act as a hydrogen bond acceptor in hydrogen bonding with dye molecules, such as with N-H bonds in methylene blue, direct red and methyl orange. Non-polar benzene rings on the dyes can also be attracted to the coffee grounds through temporary dipole-induced dipole interactions.

Magnetised *Coffea Arabica* was successfully synthesised as it displays magnetic properties. Pyrolysed coffee grounds significantly improves removing of methylene blue dye, brilliant green dye, direct red dye and methyl orange dye compared to unpyrolysed spent coffee grounds. This is probably due to an increase in surface area due to pyrolysis removing volatile substances from the coffee grounds and decomposition of cellulose and lignin which results in release of volatile products, creating pores within the coffee grounds that increase surface area and exposing more hydroxyl functional groups, allowing more Cu^{2+} ions and dye to be adsorbed. However, pyrolysed coffee grounds do not significantly improve adsorption of Cu^{2+} ions. Magnetisation of the coffee grounds generally inhibits the effectiveness of coffee grounds in removing Cu^{2+} ions and dyes to some extent, due to magnetite blocking the hydroxyl groups of the coffee grounds.

Future Work

Future experiments can be done to investigate the efficiency of adsorption of other heavy metal ions such as Iron(II), Zinc(II) and Lead(II) ions. Furthermore, reusability of pyrolysed coffee grounds after adsorption can be investigated upon more experimentation. Finally, more tests can be performed to further investigate the difference in trends between cationic dyes and anionic dyes in terms of their chemical composition to provide a reason for the difference in percentage adsorption from pyrolysed coffee grounds and unpyrolysed coffee grounds.

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Appendix

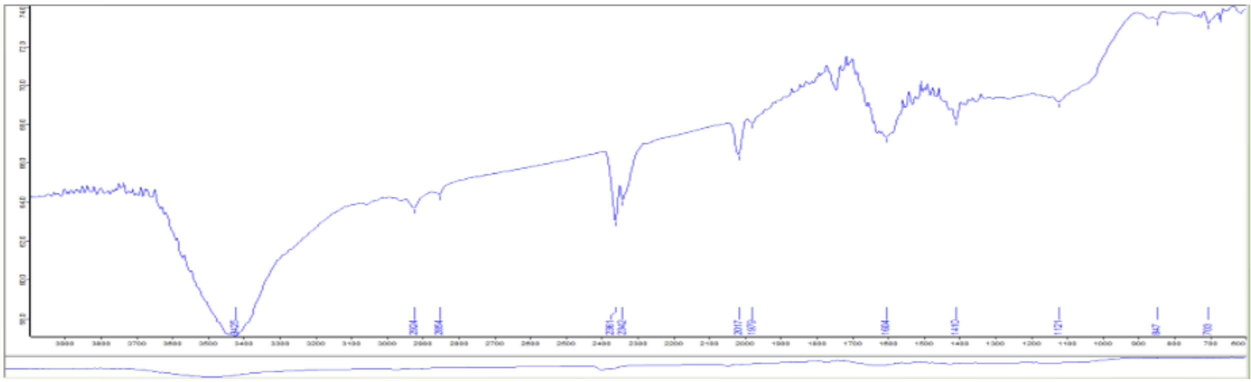

Figure 4: FTIR results for pyrolysed coffee grounds

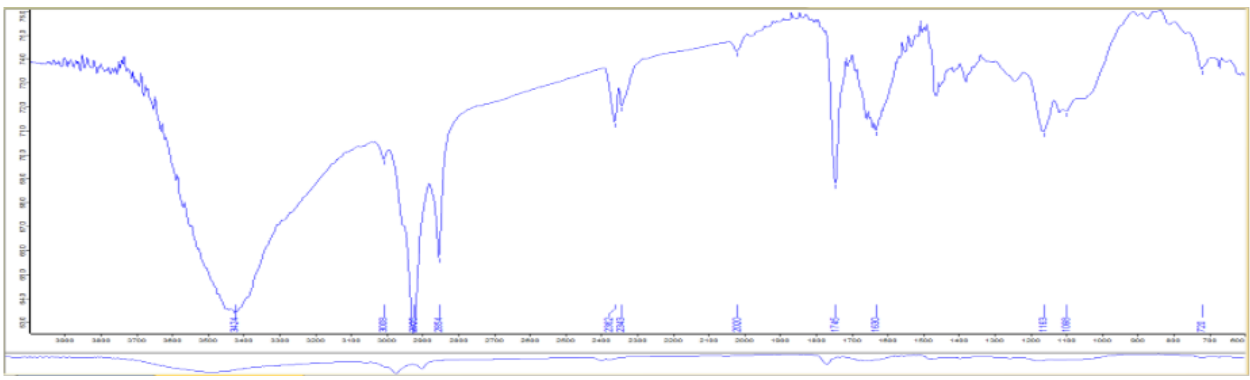

Figure 5: FTIR results for unpyrolysed coffee grounds