Synthesis of carbonised corn cobs in removal of heavy metal ions and bacteria in water purification

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Abstract

There are a lot of agricultural waste such as corn cobs found around the world and this is especially true in farming based countries. In 2019, the accumulation of agricultural waste such as corn cobs, amounted up to 2 billion tonnes worldwide and the numbers are only rising each year. This is a problem for many countries as money has to be used for the storage and removal of these wastes. In many of these countries such as China and India, heavy metal ion pollution is also prominent due to the manufacturing plants and mines in the countries. The metals which are mined may have metal dust and may be blown into the drainage and polluted the water the sewage is disposed into. In these countries, they have huge farming industries and may plant corn for biofuel and food. Corn plantation in these countries could provide the corn cobs for the carbon which would make the carbon cost-effective. Pollution of heavy metal ions may lead to heavy metal ion poisoning which could cause intellectual disability and even death. In 2013, the World Health Organization estimated that heavy metal ions poisoning resulted in 143,000 deaths, and contributed to 600,000 new cases of children with intellectual disabilities, each year. This project aims to investigate the adsorption of heavy metal ions before and after regeneration and as well as investigate the antibacterial properties of silver nanoparticles after being embedded onto the activated carbon. The steps include: Activation of carbon, Modification of carbon, Adsorption test, Regeneration of carbon, regeneration test and bacteria test. Potassium hydroxide activated carbon with a particle size of 250 micrometers (KOH250) has been discovered to have the most stable and the best adsorption results. This suggests that the carbon with the greater surface area shows the best results and that potassium hydroxide activated carbon is better in adsorbing heavy metal ions than zinc chloride activated carbon. This is consistent with the SEM imaging, where it showed to be the most porous and least amount of ash out of the four carbons. The results for the Iodine test, and adsorption tests before and after regeneration suggested that the KOH 250 carbon was the most effective in removing heavy metal ions.

1. Introduction

1.1 Literature review

There are several methods used in the water purification process, which include: (1) physical processes, such as filtration, sedimentation, or distillation; (2) biological processes, such as sand filters, active carbon; (3) chemical processes, such as flocculation, chlorination, the use of ultraviolet light.

The accumulation of agricultural waste, i.e. corncob, rice husk, rice straw, sugarcane bagasse, and wheat straw, is approximately 2 billion tons worldwide. Forest waste accounts for approximately 0.2 billion m^3; 1.7 billion tons; and industrial waste, 9.1 billion tons. Altogether, it makes more than 10 billion tons of wastes and residuals, which is a considerably huge amount; the number tends to increase over time (Dr.Salah M. El-Haggar, 2007).

Reported sources of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources. Environmental pollution is very prominent in point source areas such as mining, foundries and smelters, and other metal-based industrial operations. (Paul B Tchounwou et.al, 2014)

WHO estimated 143,000 deaths per year result from lead poisoning, with lead paint is a major contributor. Exposure contributes to 600,000 new cases of children with intellectual disabilities every year and 99 percent of children affected by high exposure to lead live in low- and middle-income countries (WHO, 2013).

China is one of the world's largest corn producers with nearly 220 million metric tons of output per year. However, farm sizes and yields differ greatly from the states. The average yield is 92 bushels per acre, and the average Chinese farmer has just 1.2 acres of land (Luis Vieira, 2015).*Escherichia coli* (abbreviated as *E. coli*) are bacteria found in the environment, foods, and intestines of people and animals. *E. coli* are a large and diverse group of bacteria. Although most strains of *E. coli* are harmless, others can make you sick. Some kinds of *E. coli* can cause diarrhea, while others cause urinary tract infections, respiratory illness and pneumonia, and other illnesses. (USGS)

Silver nanoparticles have emerged as antimicrobial agents against multidrug resistant bacteria due to their high surface-area-to-volume ratio and unique chemical and physical

properties. AgNPs have particle sizes ranging from 1 to 100 nm. The surface area-to-volume ratio of AgNPs increases as the particle size decreases. (Morones et al. 2005)

1. 2 Rational

Many methods of water purification such as ion-exchange, membrane filtration, coagulation-flocculation, flotation and electrochemical. However, these steps are overly expensive and require large amounts of energy to sustain and be operated. Corn cobs are agricultural waste which is cost efficient and is more eco-friendly as this method used organic materials for water purification. Moreover, the heavy metal ion polluted countries are mainly China and India which plant corn for food and biofuel. This further reduces the cost as corn cobs needed could be obtained locally. In wastewater and sewage water, there are also a lot of bacteria which when not treated properly, may lead to the spread of water-borne diseases. Silver nanoparticles can penetrate the membrane and enter the bacteria. There is a size-dependent antibacterial effect, namely smaller nanoparticles has a large surface area in contact with the bacterial cells and can reach the cytoplasm more often than larger nanoparticles.Interaction between silver nanoparticles and cellular structures or biomolecules will lead to bacterial dysfunction and finally death. With the silver nanoparticles embedded in the carbon, this could kill the bacteria in the water and could better prevent diseases from spreading.

1.3 Engineering Goals

- Investigate the adsorption of heavy metal ions of activated carbon.
- Investigate the antibacterial properties of modified activated carbon.
- Investigate the adsorption of heavy metal ions of carbon after regeneration.

1.4 Hypothesis

- The activating agent could increase the porosity of the carbon.
- Silver nanoparticles could be embedded onto the activated carbon
- The activated carbon could kill bacteria when embedded using chemical methods.
- The modified carbon could be regenerated after adsorption of heavy metal ions.

2. Materials and Methodology

2.1 Apparatus

Stage 1	Stage 2	Stage 3	Stage 4	Extension
Extreme Furnace	Erlenmeyer flask	Stirrers	Stirrers	Hot plate
Blender	Hot plate	Pipette	Pipette	Centrifuge machine
Sieve Shaker	Burette	Colourimeter	Colourimeter	
	Pipette		Oven	
	Erlenmeyer flask		Water Bath	

2.2 Chemicals

Stage 1	Stage 2	Stage 3	Stage 4	Extension
4M Zinc chloride	5% hydrochloric acid solution	50ppm $Fe^{3+}/Cu^{2+}/Zn^{2+}$ solution	cyclohex-anone	10M $AgNO_3$
20% Potassium Hydroxide	sodium thiosulfate	Colourimeter powder pillows	50ppm $Fe^{3+}/Cu^{2+}/Zn^{2+}$ solution	
	starch indicator	cyclohexanone		

2.3 Stage 1- Carbonise corn cobs and activation of carbon

Corn cobs were washed thoroughly using DI water and dried overnight. They are cut into small pieces. Cut up corn cobs were put into a muffle furnace at a temperature of 400 degrees Celsius for 2 hours. The resulting charcoal was crushed into small grains and sieve out the ideal size of 250 micrometers and 400 micrometers. 1 gram of different sized carbon was put into 2 containers. The carbon was treated with 30ml of 4M zinc chloride or 20% potassium hydroxide and the containers were left overnight. The carbon was washed with deionised water and filtered. The carbon was put into the furnace and was heated at a temperature of 150 degrees Celsius for 1 hours to dry. The carbon was calcined at 400 degree Celsius for 1 hour.

2.4 Stage 2: Characterization of Corn Cob Activated Carbon

2.4.1 Method 1: Iodine test

The Iodine test is a relative indicator of the porosity of the carbon. Firstly, 10ml of 5% hydrochloric acid solution was pipetted into a 250ml Erlenmeyer flask. Mixture was swirled and heated for 30s to remove excessive sulfur. The mixture was then cooled to room temperature. Then, 100 ml of 0.1M standardised Iodine solution was then pipetted into the flask. The flask was stoppered and contents were vigorously shaken for 30s. The mixture was then immediately filtered through a sheet of filter paper. Next, 50 ml of the filtrate was then pipetted into a clean 250ml Erlenmeyer flask. The filtrate was titrated with 0.1M standardised sodium thiosulfate solution until filtrate becomes pale yellow. 2ml starch indicator solution was then added and titration was continued until a colourless solution was produced. The volume of sodium thiosulfate used was recorded.

The iodine number is the X/M (mass in mg of iodine adsorbed per gram of carbon) value when the residual iodine concentration (C) is 0.05 mol dm^{-3}.

$X/M = \{(N_1 \times 126.93 \times V_1) - [(V_1 + V_{HCl})/V_F] \times (N_{Na2S2O3} \times 126.93) \times V_{Na2S2O3}\}/Mc$

$C = (N_{Na2S2O3} \times V_{Na2S2O3})/ V_F$

where N_I is the iodine solution molarity, V_I is the added volume of iodine solution, V_{HCl} is the added volume of 5% HCl, V_F is the filtrate volume used in titration, $N_{Na2S2O3}$ is the sodium thiosulfate solution molarity, $V_{Na2S2O3}$ is the consumed volume of sodium thiosulfate solution and M_C is the mass of activated carbon.

A logarithmic graph of X/M against C was plotted and the iodine value was the X/M value of 0.05.

2.5 Stage 3: Adsorption test of modified carbon

1 gram of activated carbon was put into a beaker of 50 ppm $Zn^{2+}/Cu^{2+}/Fe^{3+}$ solution and was stirred with the electric stirrer. The activated carbon was left overnight.Concentration of metal ions after removing activated carbon from the solution was measured using a colorimeter.The percentage removal of heavy metal ions could be calculated as: $(C_i-C_f)/C_i \times 100$, where

C_i - initial concentration of salt solutions (50ppm)

C_f- final reading of concentration of salt solutions

2.6 Stage 4-Chemical regeneration of exhausted activated carbon and adsorption test of recycled carbon

1g exhausted activated carbon was soaked in sodium hydroxide (25ml) (4%) in 100ml glass conical flasks. The flasks were bathed in 90°C water for 4h,while mixtures are stirred in the flasks. Activated carbon was removed from the mixture and washed under DI water for 10 minutes. Activated carbon was soaked in DI water for 1 hour. Activated carbon was dried in the oven for 1 hour at 90°C. 50 ppm of Zn^{2+}/Cu^{2+}/ Fe^{3+} were prepared in a beaker. The volume of Zn^{2+}/Cu^{2+}/Fe^{3+} salt solution was 20cm³ per gram of carbon. Activated carbon of 1 gram was put into the beaker and stirred it with the electric stirrer. It was left overnight. Concentration of metal ions was measured after removing activated carbon from the solution using a colorimeter. The concentration of the heavy metal ions before and after was compared and see how much it had managed to adsorb.

The percentage removal of heavy metal ions could be calculated as: $(C_i-C_f)/C_i$ x 100, where

C_i - initial concentration of salt solutions (50ppm)

C_f- final reading of concentration of salt solutions

2.7 Extension-Modification of the activated carbon using silver nanoparticles and bacteria test for activated carbon

2.7.1 Synthesis and impregnation of silver nanoparticles:

Peel(orange fruit) were used, and washed 2–3 times with water. 10g of peels were weighed and cut into smaller pieces. The peels were then put into 100 ml of water. The mixture was heated for 20 minutes at 60°C while stirring occasionally and then cooled at room temperature.The colour of the solution changed to yellowish brown. The mixture was then filtered using filter paper and centrifuged for 20 minutes. The solution was then stored in the refrigerator for further use. 10 mM $AgNO^3$ was mixed with the solution of peels at a ratio of 1 : 1 (v/v) to a volume of 50 mL in a flask. The flask was then wrapped with aluminum foil and heated in a water bath at 60°C for 5 hours. The solution was tested for the presence of silver nanoparticles and was poured into a 250ml beaker, and samples would be taken to put into UV-VIS to test if the solution contains silver nanoparticles. The wavelength interval where the characteristics of silver nanoparticles appear would be ranging between 400-600 nm.

The activated carbon was dipped into the solution of silver nanoparticles until the activated carbon had submerged fully into the solution which contains the silver nanoparticles to modify

the carbon. The beaker was kept in the oven and the mixture was heated gently at 50 °C until dry to remove the moisture from the mixture.

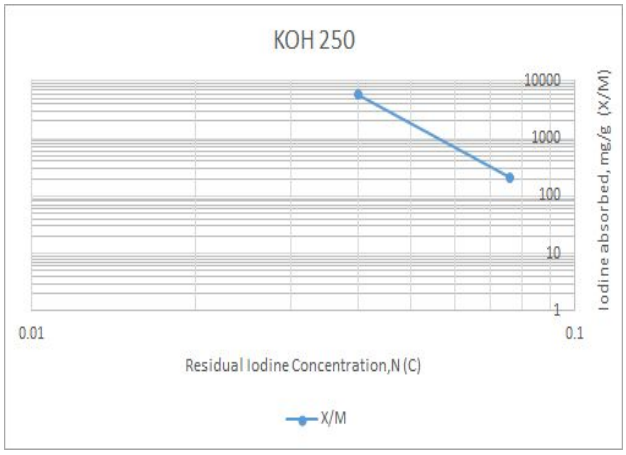
2.7.2 Bacteria test

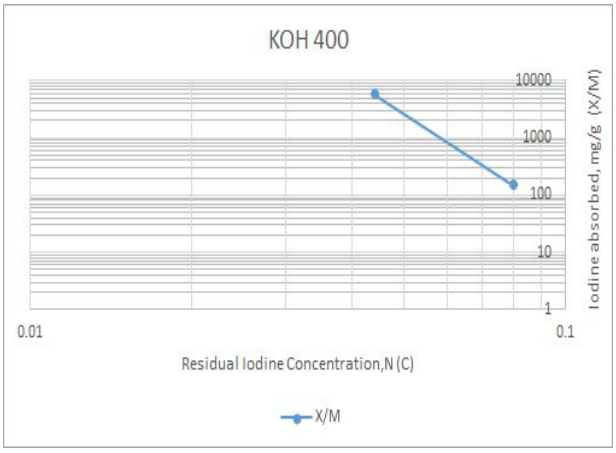
E. Coli bacteria, of the K12 597 strain, which was cultivated in Tryptic Soy Broth at 310K overnight and then centrifuged to recover the cells. The sediments were washed with DI water and resuspended in 20 cm^3 of DI water. Then, 5cm^3 of suspension was added to two tubes, one with carbon and the other as a blank. Contents of the tube were stirred for 2 min and placed in an orbital shaker. The tubes were shook in an orbital shaker at 298k with 45 rpm agitation. 10mm^3 of solution from each tube were diluted with 990mm^3 of DI water, and then the suspensions were serially diluted to determine viable cells by plating in Tryptone Soy Agar. These were the extensions that were planned to be done, but because of the time constraints, only the modification of the activated carbon using silver nanoparticles was able to be done.

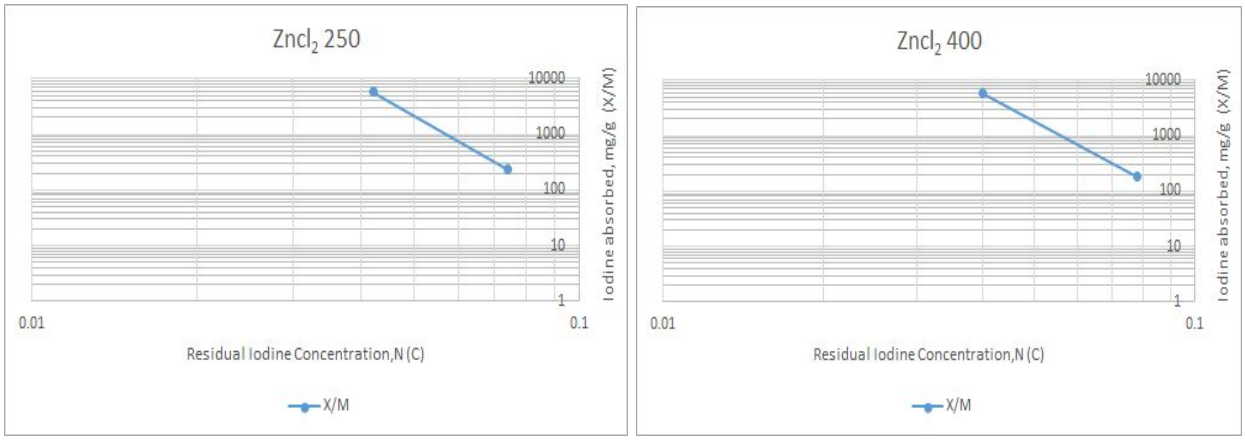
3.1 Results and analysis

Stage 2:Characterisation of activated carbon-Iodine number test

carbon(0.2g)	KOH 250	$ZnCl_2$ 250	KOH 400	$ZnCl_2$ 400
Initial burette reading /cm	0	0	0	0
Final burette reading / cm	4.4	4.0	4.0	4.2
Iodine number	1085mg/g	1110mg/g	1050mg/g	1080mg/g

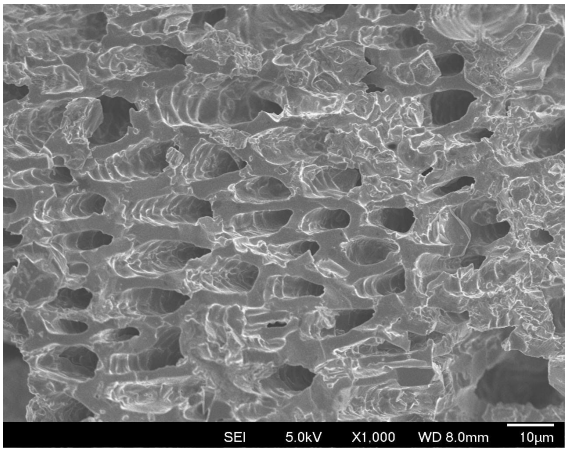




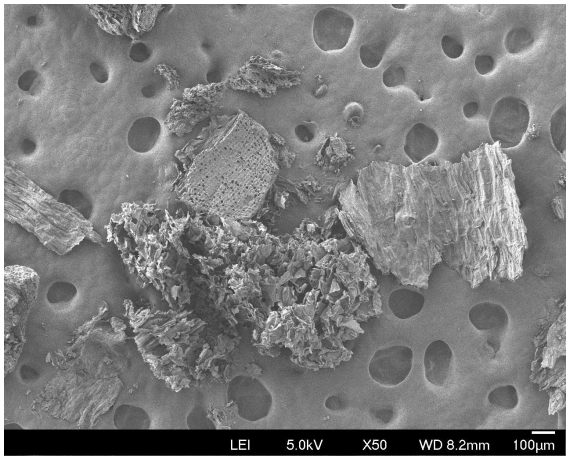


Graphs for respective carbon types, KOH 250, KOH 400, $ZnCl_2$ 250, $ZnCl_2$ 400

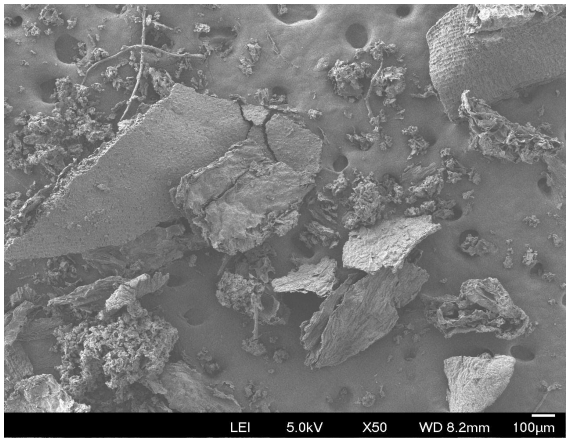
As visible from the chart and graphs, $ZnCl_2$ 250 carbon performed the best while KOH 400 carbon performed worst. Typical water treatment carbons have an iodine number ranging from 600-1450. The results were able to suggest that we are somewhere in the middle. However, due to a lack of time and materials, we were unable to do triplicate for the test. As such, we were only able to form two points which could mean that our result may be flawed.



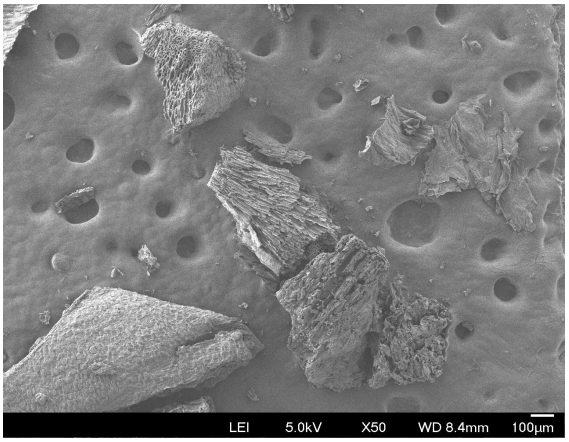
KOH 250 activated carbon



KOH 400 activated carbon



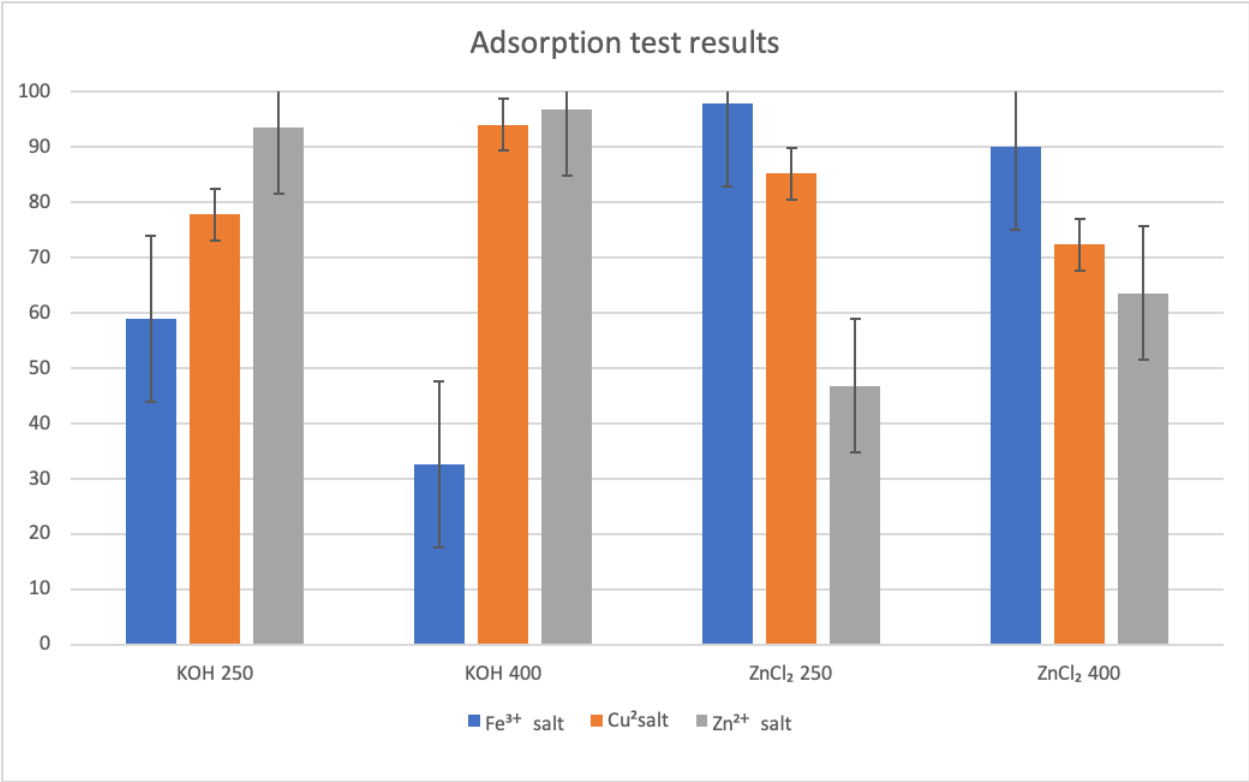
$ZnCl_2$ 250 activated carbon



$ZnCl_2$ 400 activated carbon

The SEM images of the carbon suggest that the KOH 250 activated carbon performed the best out of the four had more pores than the other activated carbon, and the pores were also closely packed, showing that it was more porous than the others. There are also less Ash particles on the activated carbon. This is thus shown from the results later that is performed the most effectively.

Stage 3: Adsorption test for activated carbon



Graph for the adsorption test results

The adsorption test results suggested that $ZnCl_2$ 250 activated carbon was the most efficient at adsorbing iron salt, while KOH 400 activated carbon was the most efficient at adsorbing zinc salts. KOH 400 activated carbon was the most efficient at adsorbing the copper salt. For the adsorption of zinc salt, the results suggest that the method of zinc chloride activation of carbon is more effective than potassium hydroxide activation. The results also suggest that in the adsorption of iron salt, potassium hydroxide activation is more effective in adsorption of iron ions. In the results, most of the adsorption for the 250 micrometer size is better than 400 micrometer carbon. This is because of the larger amount of surface area from the 250 micrometer carbon of the same mass as compared to the 400 micrometer carbon. This would increase the efficiency of adsorption as a larger surface area would increase the rate of adsorption and is able to adsorb the metal ions more effectively.

Stage 4: Chemical regeneration of exhausted activated carbon and adsorption test of recycled carbon

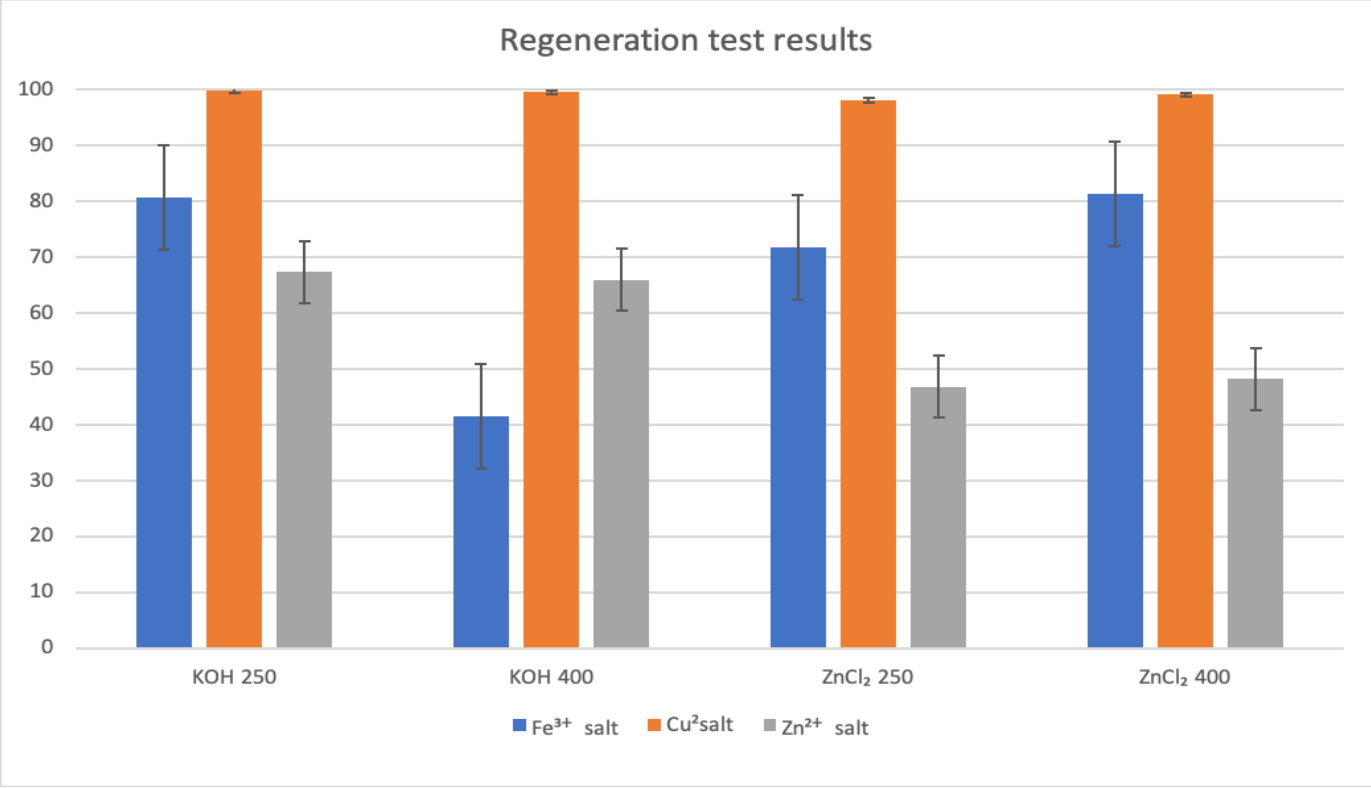


Fig. 5 Regeneration test results in a bar graph

The regeneration test results show that $ZnCl_2$ 400 regenerated activated carbon was most efficient in adsorbing iron salt. KOH 250 regenerated activated carbon was most efficient in adsorbing copper salt. KOH 250 regenerated carbon was most efficient in adsorbing zinc salt. For the adsorption of zinc salt, the results suggest that the method of potassium hydroxide activation of carbon is more effective than zinc chloride activation. The results also suggest that in the adsorption of iron salt, zinc chloride activation is more effective in adsorption of iron ions. In the results, most of the adsorption for the 250 micrometer size is better than 400 micrometer carbon. This is because of the larger amount of surface area from the 250 micrometer carbon of the same mass as compared to the 400 micrometer carbon. This would increase the efficiency of adsorption as a larger surface area would increase the rate of adsorption and is able to adsorb the metal ions more effectively. The solution has seen to change its colour to yellowish brown, and the wavelength tested was peaking at 439 nm, from the above picture of the UV-VIS results which showed the presence of silver nanoparticles. The silver nanoparticles' wavelength would usually peak at 300-540 nm when using the UV-VIS. (PeterLogeswari et.al, 2015).Verma, Rashmi &Synthesis of silver nanoparticles using plants extract and analysis of their antimicrobial propertyvolume13, Issue3, pages 311-317).

3.2 Conclusion

At the end of the experiment, it suggests that KOH 250 activated carbon showed the best results before regenerations and after regeneration. From the SEM results shown too previously ,the KOH250 activated carbon also showed the most porous and has the least Ash, which affects its adsorption abilities. The activated carbon displayed to be able to adsorb copper heavy metal ions, which was more consistent and stable after regeneration. Some possible reasons for the adsorption abilities displayed are as follows.The KOH modified carbon tends to be more microporous in research done before. This was shown also in how the SEM results showed that the KOH250 activated carbon was more porous than the others. The 250 μm activated carbon was also smaller in size, which makes the activated carbon to have a larger surface area, thus able to adsorb more heavy metal ions. The sodium hydroxide which was involved in the regeneration may have helped the activated carbon adsorption capacities to boost, causing a more stable result after regeneration. This is the application that can be used. Firstly, silver

nanoparticles modified activated carbon could be used to purify industrial wastewater as well as polluted sewage water as the modified carbon could kill bacteria in wastewater and remove potentially deadly heavy metal ions. Less-developed countries can also use this modified activated carbon for these countries are mainly based on farming which would be able to provide the agricultural waste, like corn cobs for the carbon, using the waste meaningfully for removing the dangerous heavy metal ions. This would also solve the problem of removing corn cobs using the method of burning which would produce greenhouse gases which would intensify global warming and at the same time, our method of water purification is also more eco-friendly and uses organic materials such as corn cobs and orange peels which could be easily obtained.

3.2 Future studies

We aim to further improve our process of activation so that the carbon would be more porous and could adsorb more heavy metal ions. We also aim to complete the stage of killing the bacteria so as to prove the carbon's ability of removing carbon from wastewater. If possible, we would also want to go in depth about the monolayer/multilayer adsorption of carbon and how it affects the adsorption abilities. We would also try to research the monolayer and multilayer and their benefits and cons so as to find out which one is better in different circumstances. Lastly, if we have time, we would research the properties of different carbon from different plants to see if there is any difference in their adsorption abilities and if the difference in the types of carbon affect the results.

4. References

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Appendix

1. Activation of carbonised corn cobs

Fig 1. Cutting and washing of corn cobs

Fig 2. Drying of corn cobs

Fig 3. Sieving of carbon for different pore sizes

2. Characterization of the activated carbon

3. Adsorption test

Fig 4. Process of carrying out the adsorption test with colourimeter

4. Regeneration and adsorption test for regenerated activated carbon

Fig 5. Process of carrying out the adsorption test of regenerated carbon with colourimeter

5. Extension-synthesis and impregnation of silver nanoparticles

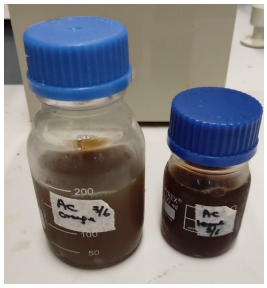

Fig 6. The completed silver nanoparticles solution(orange on the right and leaves on the left)

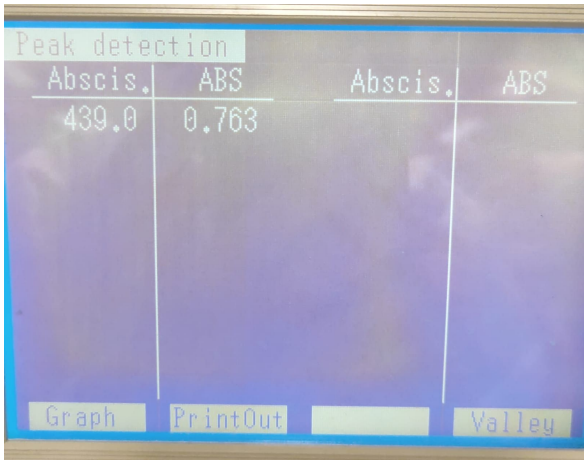

Fig 7. The wave length shown by the UV-VIS

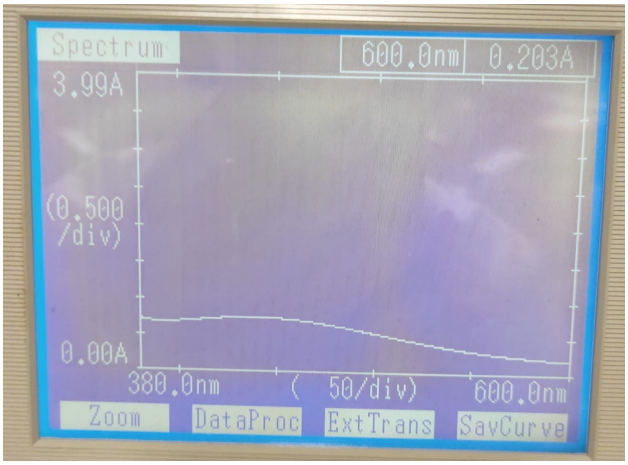

Fig 8. The graph plotted by the UV-VIS to show the wavelength of the silver nanoparticles