Removal of Chromium and Copper Ions by using Pumpkin Seeds as Adsorbent

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Abstract—**This study aimed to prepare adsorbent by using pumpkin seeds and to investigate the effectiveness between calcined and uncalcined pumpkin seeds that were physically and chemically treated to remove chromium and copper ions in aqueous solution. The uncalcined pumpkin seeds were prepared by physical (P-UC) and chemical (C-UC) treatments. In chemical treatment, the pumpkin seeds were impregnated with local vinegar to activate its active site. In both treatments, part of the pumpkin seeds was calcined at temperature 350°C (PC-350, CC-350), 450°C (PC-450, CC-450) and 550°C (PC-550, CC-550). The adsorbents were characterized by using Fourier Transform Infrared (FT-IR). Batch adsorption experiments were carried out in order to determine the effectiveness of the adsorbents in removing chromium and copper ions. The effect of adsorbent dosage, contact time and initial concentration on the adsorption process were evaluated. The final concentration of the chromium and copper ions was determined by using Atomic Absorption Spectrophotometer (AAS). The most effective pumpkin seeds as adsorbent in removing chromium ions was discovered to be C-UC at optimum condition such as 1.5g adsorbent dosage, 50mL of 50ppm initial chromium ions concentration, 700rpm speed with 30 minutes contact time since the result showed that it can remove the maximum amount of chromium ions, 68.12% compared to other types of adsorbents. Meanwhile, the most effective pumpkin seeds as adsorbent in adsorbing copper ions were revealed to be PC-550 at an optimum condition such as 1.5g dose of adsorbent, 50mL of 50ppm initial copper ions concentration, stirred for 30 minutes at 700rpm speed to remove 85.95% copper ions. The changes in FT-IR spectra of uncalcined to calcine adsorbent treatment suggested that the sorption of chromium and copper ions was consistent with the findings.**

Keywords— adsorption, agricultural waste, chromium, copper, pumpkin seeds.

I. INTRODUCTION

Industrialization is vital to global economic growth and significant contribution to human welfare. Unfortunately, with a rapid increase in industrial development nowadays, it led to large and uncontrollable industrial wastewater discharge. Most of the industrial activities such as fertilizer, chemicals, metal plating, mining and many more, discharge the industrial effluent which contains heavy metals either directly or indirectly into nature without any treatment (Fu & Wang, 2011) which can cause water pollution. Heavy metals such as copper, zinc, mercury, cadmium, lead, iron, manganese, chromium, nickel, arsenic and aluminum are non-biodegradable and considered as the most boundless contaminants found in soil and water system (Burakov et al., 2018). Heavy metals are known to be toxic, carcinogenic and can cause chemical and physical changes in the environment by altering the water quality and cause water contamination even at high or low-level concentrations.

Chromium, Cr is a type of heavy metal that is mainly use in chrome plating, metal ceramics and in alloys industry. Health hazards from chromium associated with the level of exposure such as consuming high levels of chromium in polluted water or inhaling fumes from heated chromium can cause upset stomachs and ulcers, kidney and liver damage, respiratory problems, cancer and death (National Institutes of Health, 2018). Copper, Cu is widely used in manufacture of electrical wire. Copper is an essential nutrient needed in a small amount to prevent anaemia and keep the skeletal, reproductive and nervous system healthy. Overexposure of copper can cause chronic diseases such as liver failure, hepatic, renal disease and haemolytic anaemia (Baker et al., 2007).

Currently, there are numerous conventional treatment technologies to expel heavy metals for example, chemical precipitation, ion exchange, oxidation, reduction, reverse osmosis, electrodialysis, ultrafiltration, coagulation-flocculation, membrane filtration, membrane separation, electrochemical operation and solvent extraction. However, some of these methods have several limitations such as costly, low removal efficiency, ineffective at low level of metal ion concentration, slow process, high energy consumptions and produce a large quantity of sludge (Wang & Chen, 2009)

On the other hand, adsorption is an efficient and inexpensive technique for removing deadly heavy metal ions from wastewater effluent. Besides, adsorption also well known for its selectivity and viability even on an extremely low-level concentration of contaminants (Kurniawan et al., 2011). Adsorption also has been recognized for its simplicity, cost effectiveness, easy recovery, regeneration limit and sludge free activity (L. Zhang, et al., 2016). However, the cost for conventional adsorbents such as activated carbon is costly and requires additives to improve its efficiency.

Thus, recent studies focus in using agriculture waste to replace conventional adsorbent to remove heavy metals ions from industrial wastewater. This is to reduce the cost on adsorbent. Many studies have shown promising potential on removal of heavy metal using agricultural waste such as rice husk (Masoud et al., 2016; Shalaby et al., 2017), jackfruit peel (Ranasinghe et al., 2018), grape seed (Okman et al., 2014), grape bagasse (Demiral, 2016), corn stalk (K. Zhang & Chen, 2018), cherry kernels (Vukelic et al., 2018), persimmon leaves (Lee & Choi, 2018) and durian shell (Kurniawan et al., 2011).

There was a recent study that explored the possibility of pumpkin seed hull as a promising adsorbent in removing discharge of toxic pesticides such as 2,4-dichlorophenoyacetic acid from wastewater (Njoku et al., 2013). However, there is no recent study found on using pumpkin seed as a low cost adsorbent in removing heavy metals found in wastewater. Thus, this research explores the potential of pumpkin seeds as a minimal cost adsorbent in removing chromium and copper ions that are commonly found in wastewater. In this work, pumpkin seeds were used as a precursor for adsorbent prepared by physical and chemical treatment. The effects of adsorbent dosage, initial heavy metal concentration and contact time on the percentage of heavy metal removed were investigated.

II. METHODOLOGY

A. Preparation of Adsorbate

Analytical grade of Potassium Dichromate, $K_2Cr_2O_2$ and Copper (II) Sulphate Pentahydrate, $CuSO_4.5H_2O$ purchased from PC Laboratory (M) Sdn. Bhd were chosen as model adsorbate. The standard stock solution, 1000ppm of $K_2Cr_2O_2$ and $CuSO_4.5H_2O$ were prepared. Different initial concentration such as 50ppm, 70ppm and 100ppm were prepared by dilution with distilled water.

B. Preparation of Adsorbent

Pumpkins, *Cucurbita moshata* types were bought from a local market. The pumpkins were cut into half to collect the pumpkin seeds. The collected pumpkin seeds, PS were continued for further treatment such as physical and chemical treatment.

In the physical treatment, PS was washed a few times with distilled water pursued by deionized water at the end. This step is essential to remove any physical impurities and dirt that adhered on the surface of pumpkin seeds. The cleaned PS were scattered evenly on the aluminium tray surface to avoid multiple stacking and to ensure uniform drying of the cleaned PS. Also, the surface of aluminium tray being used must be in a clean condition to avoid contamination. The cleaned PS were oven dried at 70°C for 24 hours (Njoku et al., 2013). The oven used was a medium size, Froilabo (SN: 505137) laboratory microwave oven. The dried PS was crushed and ground to smaller particle sizes using Waring (SN:8011ES) laboratory grinder. The PS was sieved to obtain particle size less than 500micron using Endecotts Octagon 2000 Digital Sieve Shaker. The sieved PS was stored in an airtight container for further usage and referred to as "physical-uncalcined" (P-UC). Part of the sieved PS was used for calcined physical treatment. This is a carbonization step where the PS was carbonized at temperature 350°C, 450°C and 550°C for 1 hour in Carbolite (Model: ELF 11/14B) front-loading furnace. This type of pumpkin seeds sample is referred to as "physically calcined-calcination temperature" (PC-350, PC-450, PC-550).

Meanwhile, in the chemical treatment, the initial steps for chemical treatment were the same as the physical treatment where the PS was washed several times with distilled water, oven dried, crushed and ground. Then, local vinegar (acetic acid) was used, as vinegar is a low cost material and easily available in the market. The dried PS was mixed with Tesco's vinegar with PS and vinegar ratio of 1:5 (mass:volume) in a beaker sealed with aluminum foil for 24 hours in the laboratory at standard room temperature. Then, the mixtures were filtered using a local household filter. The solid residues on the filter were scattered evenly on aluminum tray, dehydrated in the microwave oven at 105°C for 15 hours until the PS was dried. The dehydrated PS was washed with distilled water and 0.1M sodium hydroxide, NaOH solution until the pH of the washing solution reach pH 6.5 to 7.5. This step was to neutralize the acidic PS. The neutralized PS was oven dried again at 105°C for 24 hours. The dried PS was crushed, pounded and sieved to obtain less than 500micron particle size. The sieved PS was kept in airtight container. The PS samples were labelled as "chemical-uncalcined" (C-UC). On the other hand, after the impregnated samples were sieved, part of the activated PS was calcined at temperature 350°C, 450°C and 550°C for 1 hour. Lastly, the activated PS char was stored in an airtight container and referred to as "chemically calcined-calcination temperature" (CC-350, CC-450, CC-550).

C. Characterization of Adsorbent

All the eight types of adsorbents prepared from physical and chemical treatments were analysed to determine its characteristics. The chemical functional groups of the adsorbents were determined by using Fourier Transform Infrared (FT-IR) spectroscopy. The porosity of adsorbents was supposed to be analysed by using Brunauer-Emmet-Teller (BET) equipment, however the equipment was broken during the analysis.

D. Batch Adsorption Experiment

The batch adsorption experiments were conducted by putting 50mL of aqueous metal solutions in Erlenmeyer flask. The mixture of adsorbent in the solution was stirred using magnetic stirrer at 700rpm stirring speed for 30 minutes. To determine the effect of adsorbent dosage, the experiments were carried out by manipulating dose of adsorbent at 0.5g, 1.0g and 1.5g. Next, the contact time for each type of adsorbents were maintained for 120 minutes while the concentration of the 100mL solution was kept constant at 50ppm and 1.0g adsorbent in order to investigate the effect of contact time. Lastly, the effect of initial adsorbate concentration on the percentage of removal was investigated by varying the initial concentration at 50ppm, 70ppm and 100ppm using 0.5g adsorbent. The final concentration of metal ions was determined by using Atomic Absorption Spectrophotometer (AAS). The same experimental steps were triplicated for eight types of adsorbents prepared to remove chromium and copper ions.

III. RESULTS AND DISCUSSION

A. Characterization of Adsorbent

Based on Fig. 3 FT-IR analysis chart, the stretch peaks at 2922 cm^{-1} and 2853 cm^{-1} are assigned to C-H stretching of methyl groups (Njoku et al., 2013). The peak at 1743 cm^{-1}, 1710 cm^{-1} and 1652 cm^{-1} are corresponded to C=O derivatives such as ester, carboxylic acid and amide respectively. The medium intensity peaks at 1545 cm^{-1} and 1455 cm^{-1} are attributed to aromatic C=C functionality. The band at 1160 cm^{-1} can be due to C-N stretch derivatives such as amines.

For PC-350 chart in Fig 3., the peak at 1712 cm^{-1} indicates the C=O derivatives such as ketone and 1156 cm^{-1} can be occurrence of C-N stretch derivatives such as amines. Not a single peak was found in the FT-IR analysis of PC-450. In PC-550, the medium intensity peak at 3649 cm^{-1} is referred to as free O-H bond.

In Fig. 4, the two peaks in C-UC are referred to as C-H stretching of methyl groups (Njoku et al., 2013). The peak at 1742 cm^{-1} is ascribed to C=C derivatives for ester compound (Pavia et al., 2001), 1631 cm^{-1} is noted as C=O derivatives for amide ,1544 cm^{-1} and 1456 cm^{-1} are absorption bands for aromatic C=C bond (Pavia et al., 2001), 1375 cm^{-1} is referred to as $-CH_3$ with bending absorption (Pavia et al., 2001), 1160 cm^{-1} frequency is noted as C-N derivatives that are also found in the P-UC chart, 1096 cm^{-1} and 722 cm^{-1} is considered as C-OH stretching and C-O-H vibration respectively (Njoku et al., 2013).

For CC-350, a short peak at 2970 cm^{-1} is noted as C-H derivative for aldehyde, 1738 cm^{-1} is a very strong band for ester in C=O groups, 1365 cm^{-1} is referred to as $-C(CH_3)_3$ group while the two twin peak at 1228 cm^{-1} and 1217 cm^{-1} can be attributed to the presence of amines in C-N derivatives (Pavia et al., 2001). In the CC-450, more peaks were found such as at 3455 cm^{-1} is an O-H structure for H- bridge while the next peak at frequency 2948 cm^{-1}, 3016 cm^{-1} and 2970 cm^{-1} is an O-H structure for chelate H- bridge (Pavia et al., 2001), 1738 cm^{-1} is ester in C=O groups, 1435 cm^{-1} is noted as $-CH_3$ group, 1365 cm^{-1} is related to $C(CH_3)_3$, 1228 cm^{-1} and 1216 cm^{-1} show the presence of amines and 1092 cm^{-1} can be referred to as C-OH stretching frequency. The vibration bands observed at 896 cm^{-1} and 770 cm^{-1} can be related to vibrations associated to ring structures (Díaz-muñoz et al., 2016). The peak observed at 539 cm^{-1} and 527 cm^{-1} can be due to the presence of compound containing halogen, which in this case is C-Br, an aliphatic bromides. Lastly, the same structure is found in the CC-550 chart in Fig. 4.

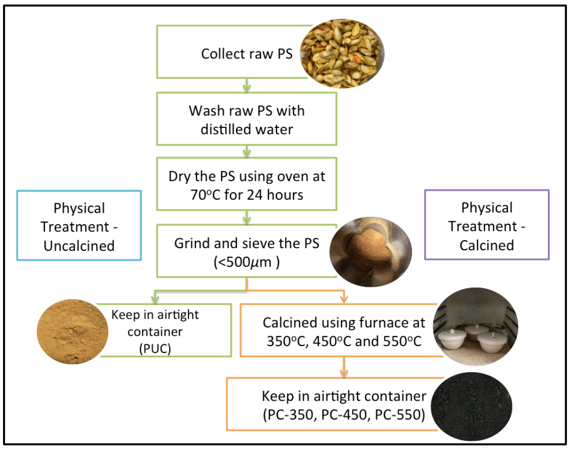

Fig. 1: Preparation of pumpkin seeds as adsorbent by physical treatment.

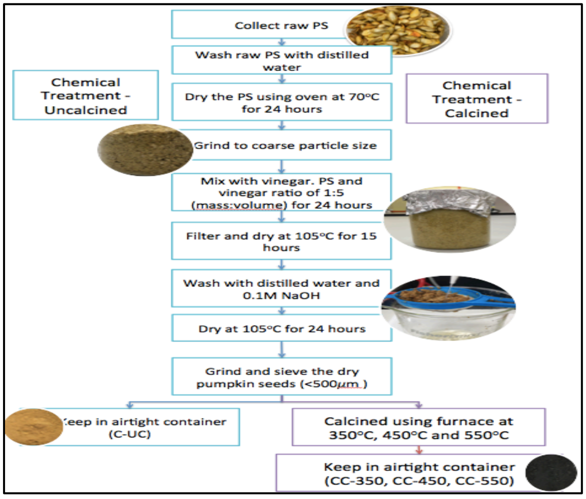

Fig. 2: Preparation of pumpkin seeds as adsorbent by chemical treatment.

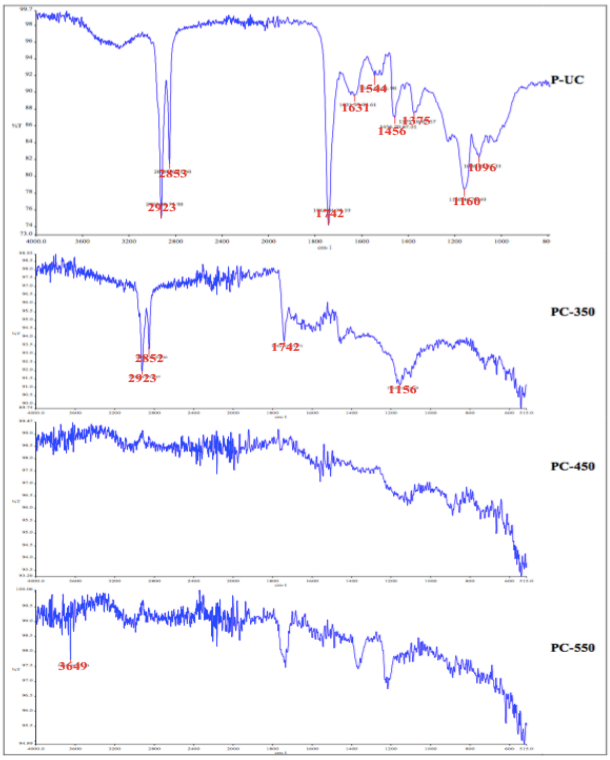

Fig. 3: FT-IR chart for the physically treated adsorbent.

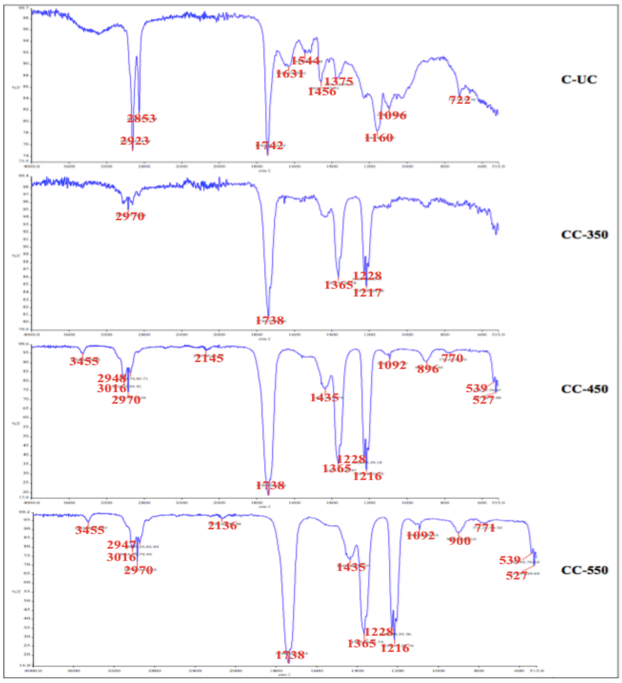

Fig. 4: FT-IR chart for the chemically treated adsorbent.

B. *Effect of Adsorbent Dosage*

Based on Fig. 5, it was found that as the dosage of adsorbent increased, the percentage of chromium ions removed was increased. The maximum chromium ions removal at 1.5g dose of adsorbent for physically treated adsorbent was 65.44% by using PC-550 while for chemically treated adsorbent, the maximum chromium ions removal was 68.12% by using C-UC. The percentage of removal of both C-UC and PC-550 does not have significant difference. Hence, C-UC is more preferable as compared to PC-550. This is because C-UC only requires chemical treatment without to be calcined at high temperature. High calcination temperature uses more energy, thus increasing cost. The cost for chemical such as vinegar that is used in this research is lesser than the cost for high energy consumption. For physically and chemically treated adsorbent, it was found out that the PS that was calcined at the highest temperature of 550°C was more effective compared to 350°C. This is due to the temperature is not high enough to activate the adsorption sites on the adsorbent surface.

According to Fig. 6, the maximum copper ions removal was 85.95% by using PC-550 and 82.17% by using CC-450 at 1.5g adsorbent dosages. It was found that as the dose of adsorbent increased, the percentage of copper ions removed was increased because of accessibility of more attaching sites present on the adsorbent. However, same scenario happened for physically and chemically treated adsorbent used to remove chromium and copper ions where further addition of adsorbent dosage does not substantially increase the sorption yield due to where binding of relatively all chromium ions to the adsorbent area and the formation of equilibrium between chromium or copper ions on the adsorbent and in the solution (Kumar, Kumar, & Sinha, 2014).

C. *Effect of Contact Time*

Based on Fig. 7, for physically and chemically treated adsorbent, the maximum chromium ions removal after 120 minutes was 61.83% and 60.99% by using PC-550 and C-UC respectively. As shown in Fig. 8, the maximum copper ions removal after 120 minutes was 75.97% and 84.53% by utilizing PC-450 and CC-450 respectively.

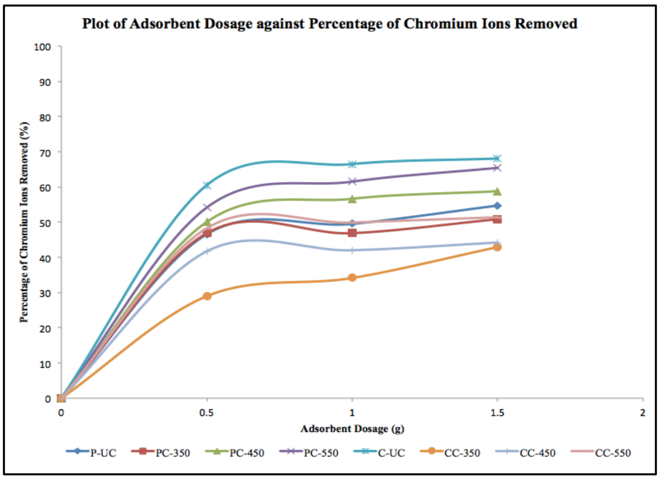

Fig. 5: Graph of adsorbent dosage against percentage of chromium ions removed using physically and chemically treated adsorbent.

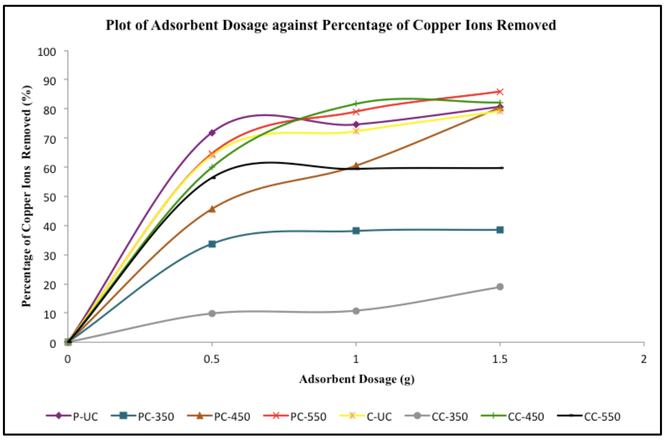

Fig. 6: Graph of adsorbent dosage against percentage of copper ions removed using physically and chemically treated adsorbent.

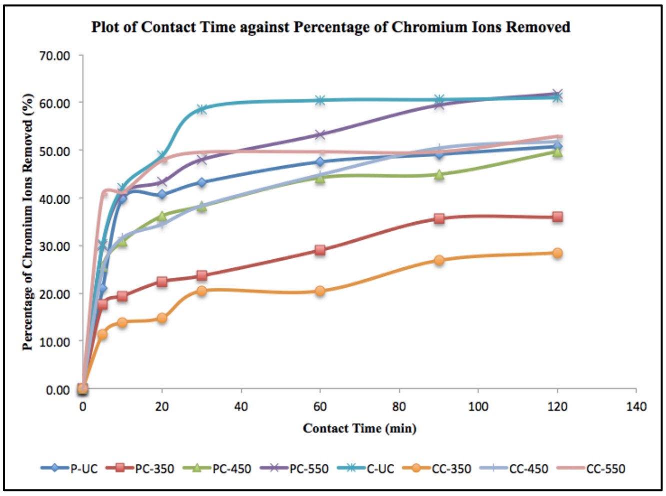

Fig. 7: Graph of contact time against percentage of chromium ions removed using physically and chemically treated adsorbent.

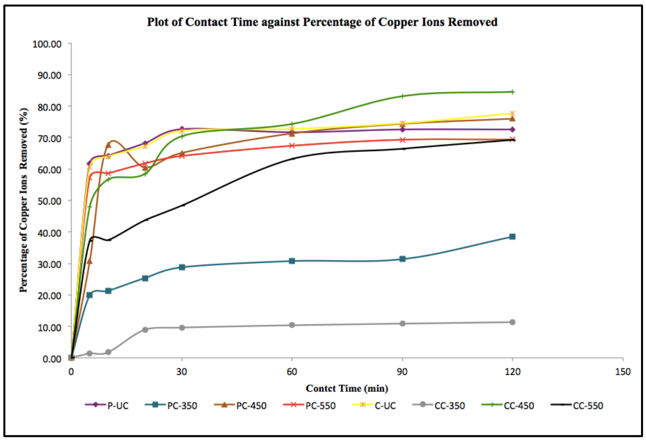

Fig. 8: Graph of contact time against percentage of copper ions removed using physically and chemically treated adsorbent.

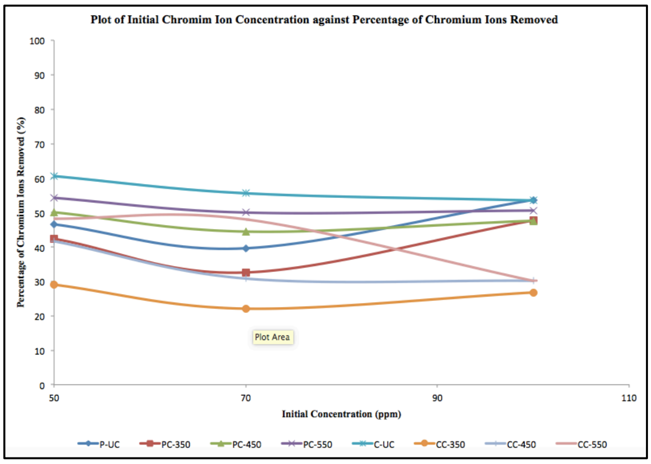

Fig. 9: Graph of initial concentration of chromium ions against percentage of chromium ions removed using physically and chemically treated adsorbent.

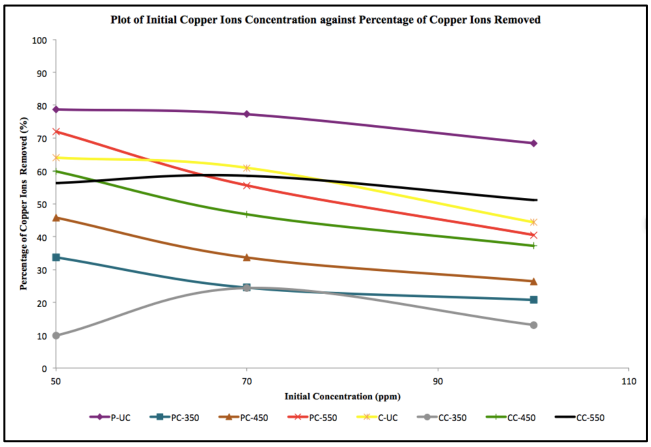

Fig. 10: Graph of initial concentration of copper ions against percentage of copper ions removed using physically and chemically treated adsorbent.

Adsorption behaviour was observed and associated to the fact that initially the adsorption of chromium or copper ions onto the adsorbent surface was rapid within the first 5 minutes due to the active sites are abundantly available on the surface of the adsorbent. As the active sites on the adsorbents are progressively being spent with time, the adsorption process turns out to be slow and achieves a steady and equilibrium stage after a certain time interval. This is credited to the decrease in the driving force after a certain period of operation (Ravulapalli & Kunta, 2018).

D. Effect of Initial Concentration

As shown in Fig. 9, it is noticed that with increment in the initial concentration of chromium ions from 50ppm to 100ppm, the maximum percentage of chromium ions removed by using physically treated adsorbent was decreased from 54.16% to 50.56% for PC-550. While for chemically treated adsorbent, the maximum percentage of removal decreased from 60.53% to 53.48% for C-UC. At high concentration, there is no significant difference between C-UC and P-UC in removing chromium ions. The preparation of adsorbents by physical treatment without calcination process is more cost saving. However, in order to gain more effective chromium removal results, uncalcined chemical treatment is more preferable. Besides, the cost for chemical that is used such as vinegar is cheap and easily available.

Based on Fig. 10, the percentage of copper ions removed decreased as the initial concentration was increased from 50ppm to 100ppm such as from 78.72% to 68.43% for physically treated, P-UC and 56.38% to 51.13% for chemically treated adsorbent, CC-550. The result of CC-350 showed that the amount of copper ions removed is too small, hence it is inappropriate to refer it as removal probably due to copper ions lost to surrounding by vaporization or the calcination temperature is too low.

As the initial concentration increased, the percentage of removal decreased. This is due to at lower concentration, more chromium or copper ions in the solution would react with the binding sites on the adsorbents thus facilitated the maximum removal. At higher concentration, more chromium or copper ions left unsorbed in the solution due to the saturation of the binding sites. This suggests that the energetically less favourable sites are involved with increase chromium or copper ions concentration in aqueous solution (Kumar et al., 2014).

IV. CONCLUSIONS

This study had successfully demonstrated the preparation of pumpkin seeds as adsorbent and its effectiveness in removing chromium and copper ions using uncalcined and calcined pumpkin seeds that were prepared by physical and chemical treatment. Based on the adsorption experiments performed and discussed, the most effective adsorbent in removing chromium ions between uncalcined and calcined physical treatment was found to be PC-550 with 1.5g dosage, 50mL of 50ppm initial chromium concentration, stirred for 30 minutes at 700rpm speed. While the most effective adsorbent in removing copper ions between uncalcined and calcined physical treatment was PC-550 with 1.5g dosage, 50mL of 50ppm initial copper ions concentration, stirred for 30 minutes at 700rpm speed.

Then, for chemical treatment, the most effective adsorbent in removing chromium ions between uncalcined and calcined was found to be C-UC with 1.5g dosage, 50mL of 50ppm initial chromium concentration, stirred for 30 minutes at 700rpm speed. Meanwhile, the most effective adsorbent in removing copper ions between uncalcined and calcined chemical treatment was CC-450 with 1.0g dosage, 100mL of 50ppm initial copper ions concentration, stirred for 120 minutes at 700rpm speed.

Among all, the most effective adsorbent in removing chromium ions was C-UC at optimum condition such as 1.5g adsorbent dosage, 50mL of 50ppm initial chromium ions concentration, 700rpm speed with 30 minutes contact time since the result showed that it can removed the maximum amount of chromium ions, 68.12% compared to other types of adsorbents. On the other hand, the most effective adsorbent in adsorbing copper ions was PC-550 at optimum condition such as 1.5g dose of adsorbent, 50mL of 50ppm initial copper ions concentration, stirred for 30 minutes at 700rpm speed to remove 85.95% copper ions.

The changes in FT-IR spectra uncalcined to calcine adsorbent treatment suggests that the metal sorption of chromium and copper ions to the oxidation of surface functional group and a possible complexion reaction between metals and those structure found in the adsorbent is reported to be consistent with the result obtained. The adsorbents used can be studied whether it can be treated to be reused again to remove various types of heavy metals in the future research.

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