Removal of Al(III) and Cu(II) from Textile Wastewater using Activated Carbon Prepared from Rubberwood Sawdust and Kenaf Core Fiber

Nik Raihan Nik Yusoff*, Mohd Shafiq Shamsuddin, Mohd Zazmiezi Mohd Alias, Rozidaini Mohd Ghazi, Nor Shahirul Umirah Idris

Faculty of Earth Science, Universiti Malaysia Kelantan, Jeli Campus, 17600 Jeli, Kelantan, Malaysia

Abstract

This study reports on the use of activated carbon prepared from rubberwood sawdust and kenaf core fiber, as an adsorbent for the removal of aluminum, Al(III) and copper, Cu(II) in textile wastewater. Rubberwood activated carbon (RWAC) and kenaf core fiber activated carbon (KFAC) were prepared by chemical activation using 10%w/w - 60%w/w of phosphoric acid (H_3PO_4) loading. Adsorption experiments for both activated carbons were performed on the effect of contact time, pH, and dosage of activated carbon used. The best RWAC and KFAC were obtained by 40% and 30% loading of H_3PO_4 with a BET surface area of 303.65 m^2/g and 361.22 m^2/g respectively. This has been approved by the FESEM images of well-developed pores observed on the surface of both activated carbons. FTIR spectra show some functional group intensity becomes less, more or shift to a higher or lower frequency level, even disappeared after carbonization and activation process. The maximum Al(III) and Cu(II) removal were achieved using KFAC with 83.5% and 73.5% removal, respectively at pH 11 with 2.0 g of activated carbon dosage after 120 minutes of contact time. This study indicated that the prepared activated carbon able to remove the heavy metal in the textile wastewater.

Keywords: Rubberwood sawdust, kenaf fiber, activated carbon, aluminum (III), copper(II)

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*Corresponding author: Nik Raihan Nik Yusoff; email: nraihan@umk.edu.my

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Introduction

The textile industry generates substantial volumes of water (400 l/kg of fabric) mixed with chemicals associated with the dyeing process [1]. Chemical compositions of the reagent used in textile industries are diverse ranging from inorganic to organic. Most of the disposed dyes are toxic and potentially carcinogenic and their removal from industrial effluent is should be highly concerned [2]. These toxic and allergic metals based dye, usually from cadmium, copper, nickel, zinc, and compounds like formaldehyde and chlorinated hydrocarbon used in many textile productions. They can penetrate the textile during the production process especially dyeing process and color fixation. These sources of pollution have become a major hazard issue due to their possible toxic effects.

The treatment of wastewater from the textile industry has become a popular issue in Asia countries. Many technologies have been developed for purification and treatment of wastewater such as ion exchange, phytoremediation [3,4], osmosis, catalyst [5-7], bacteria bio-flocculants, and nanofiltration [8]. Most of these treatment techniques could not be implemented by small-scale industry due to the involvement of capital cost with continual expenses [9]. Studies of heavy metal removal from dye-containing wastewater have revealed that adsorption using activated carbon to be effective among the physicochemical processes [10]. This statement has been supported by recent studies where activated carbon can be utilized at industrial waste and food manufacturing [11-13].

In the present study, rubberwood sawdust (RWSD) and kenaf core fiber (KCF) have been applied as a precursor for chemical activated carbon. The final products were used for heavy metal adsorption study.

Materials and Methods

Wastewater collection

Textile wastewater was collected from the local batik factory in Kota Bharu, Kelantan. The wastewater used for this study was collected from the dyeing, soaking, and washing process of batik textile production. The collected sample was stored in a polyethylene container preserved according to standard method procedures [14]. Aluminum(III) and copper(II) which contain in the textile wastewater were the main adsorbates to be removed using the adsorption process by produced activated carbon in this research.

Preparation of activated carbon

Raw materials were collected from local rubber sawmill and National Kenaf and Tobacco Board in Kota Bharu, Kelantan, Malaysia. The raw materials were washed with water and dried for 24 hours in an oven at a temperature of 105°C. Next, the dried materials were cut and ground before sieved to the size of 500-600 µm. The materials were pre-carbonized at 400°C with 1 hour holding time in a closed system. The resulting chars were subsequently impregnated with impregnation ratios (IR) of 1:4 (w/w) using different loading of 1.0 M H_3PO_4 (10 %, 20 %, 30 %, 40 %, 50 %, and 60 %) for 24 hours. The excess H_3PO_4 was latter filtered using a vacuum pump and the samples were left to dry overnight in an oven at 105°C. The samples were then carbonized at 500°C using an electric muffle furnace (Model: JSMF-30T). The activated carbons were then dried in an oven at 105°C for 24 hours. This preparation method of activated carbon was adopted from our previous study [15]. Finally, activated carbon with a particle size of 200-300 µm was obtained by further crushing and sieving process in the final step. The activated carbon produced for RWSD and KCF was denoted as RWAC and KFAC, respectively throughout the work.

Activated Carbon Characterization

RWAC and KFAC were characterized to identify the best surface area and porosity using N_2 adsorption isotherm of BET surface area analyzer based on different impregnation of acid concentration of H_3PO_4 applied. The activated carbons sample was characterized by field emission scanning electron microscopy (FESEM) and Fourier-transform infrared (FTIR) spectroscopy. FESEM analysis was used to illustrate the surface morphology of the activated carbons samples. FTIR analysis was conducted to find out the surface functional groups on the activated sample.

Adsorption Experiment

The batch experiment was carried out using three variables: pH (3, 5, 7, 9, 11), contact time (0-180 min), and sorbent dosages (0.4 g - 2.0 g). For each conducted experiment, 50 ml of textile wastewater samples were contained in 100 ml Erlenmeyer flasks. The concentration used for the study was set according to the concentration of metal from industrial discharge. Different amounts of adsorbents were added into flasks with a wastewater sample and the solution pH was adjusted using 1.0 M NaOH and 1.0 M HCl. The experiments were carried out in orbital shaker at 150 rpm. The sample solutions were withdrawn every 30 minutes and residual concentrations were determined. The solutions were filtered using a GF/C glass microfiber filter prior to analysis. The heavy metal concentrations remaining in the treated solution were measured using Atomic Absorption Spectrophotometer (AAS) (Model Perkin Elmer- 3100, Japan).

Results and Discussions

Characterization of activated carbon

Effect of H_3PO_4 activation on the surface area and porosity of activated carbon

Activating agents play a vital role in the development of pores structure and surface area. Both activated carbon (RWAC and KFAC) were activated by different loading of H_3PO_4 (10%, 20%, 30%, 40%, 50%, and 60%). The surface area of ACs was analyzed using nitrogen adsorption. The BET surface area of RWAC and KFAC was shown in Fig. 1. The RWAC recorded enhancement of BET surface area from 166.68 m^2/g to 303.65 m^2/g parallel with increasing acid loading from 10 % to 40 % however declined to 288.56 m^2/g at 60% of acid loading. The BET surface area of KFAC that shown in Fig. 1 was enhanced from 256.43 m^2/g to 361.22 m^2/g as acid loading increased from 10 % to 30 % and started to decrease at 40% of acid loading with lowest BET surface area of 180.05 m^2/g at 60% of acid loading.

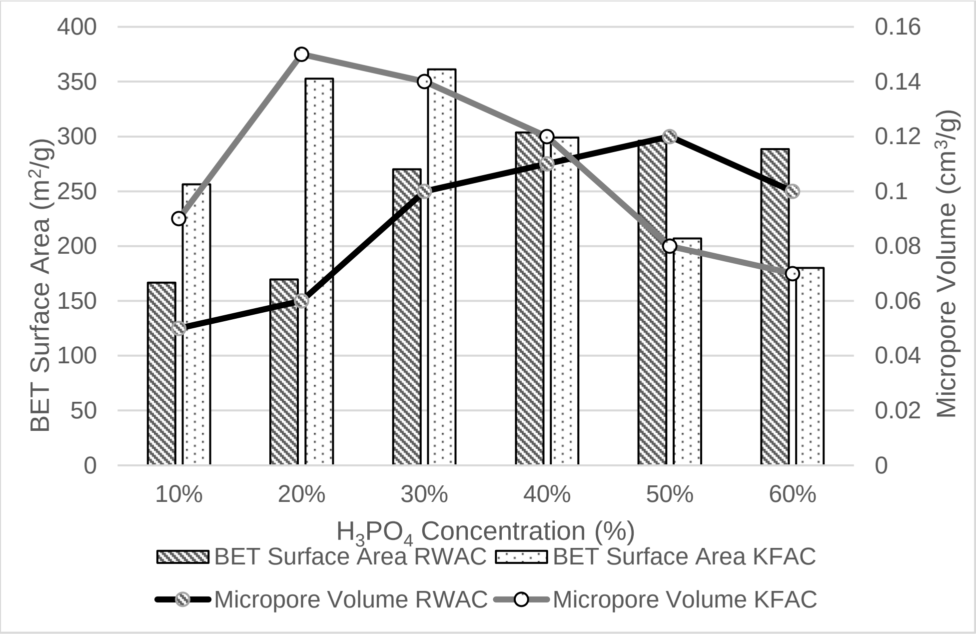

Fig. 1 Effect of H_3PO_4 concentrations on BET surface area of RWAC and KFAC

It was noted that AC produced from RWSD has a higher surface area and micropore volume than AC produced from KCF. This phenomenon may be due to the difference in the chemical composition of raw materials [16]. However, the declining value of the surface area and micropore volume in KFAC at 60 % of H_3PO_4 could be attributed to one or a combination of reasons such as pore blockage by oxygen surface groups that produced by acid, electrostatic repulsion of surface probe molecules (nitrogen) and wall erosion or destruction of micropore walls by liquid oxidants [16]. Hence, RWAC and KFAC that activated with 40 % and 30 % of H_3PO_4 respectively were used for adsorption experiments.

FESEM analysis

The morphology of RWSD and KCF from FESEM images was shown in Fig. 2 (a) and (b) respectively. The surface of both raw materials was curly form, highly packed, little pores on the surface, and no cavities were observed. This observation was similar with the previous study [17]. It was observed that after carbonization at 400 °C, the surface of char for both raw materials possesses more asymmetrical pores due to the decomposition of volatile matter [18]. This was supported by the previous study carried out by Thanapal et al, [19], where larger surface area was created from the increasing degree of porosity after the carbonization process. In addition, these holes formation was enhanced by the disintegration of volatile matter from biomass. Activation with H_3PO_4 at 500 °C has shown progressive changes on the surface with higher pores development.

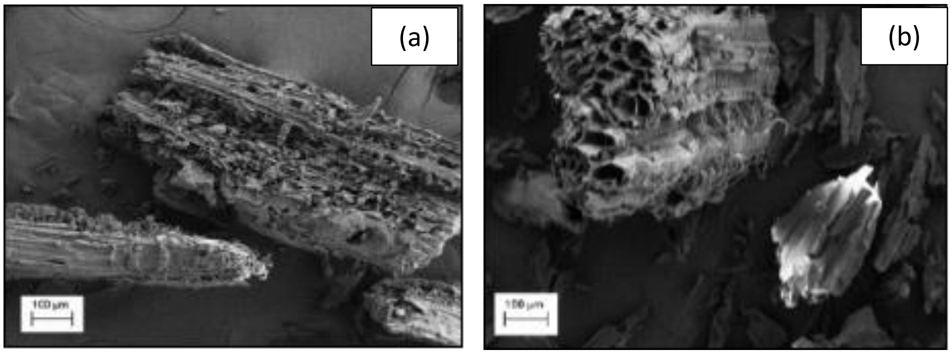

Fig. 2 FESEM micrograph of (a) RWSD and (b) KCF at 100x magnification

Pores developed in the char of KCF and RWSD promoted the diffusion of an activating agent into the cavities consequently enhancing the H_3PO_4-carbon reaction through acid hydrolysis processes. This event latter would create more pores [20]. Images of KFAC and RWAC as shown in Fig. 3 (a) and (b) respectively were parallel with the justification discussed.

Moreover, the presence of H_3PO_4 with dehydrogenation properties in the interior of the precursor can restrict the formation of tar species and reduce the production of other volatile products [21]. The activating agent applied disintegrates the polymeric structure of parent carbon and resulted in the leftover of stiff carbon skeleton in the form of aromatic sheets and strips [22].

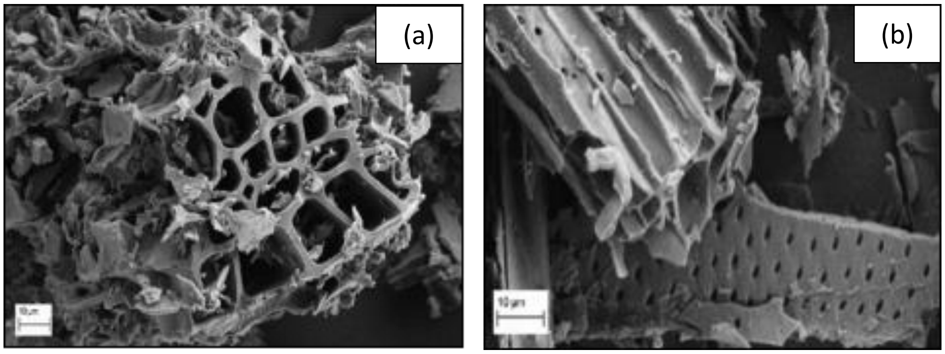

Fig. 3 FESEM micrograph of (a) RWAC (40% H_3PO_4) and (b) KFAC (30% H_3PO_4) at 2000x magnification

FTIR analysis

FTIR spectra for RWSD demonstrated in Fig. 4 displayed major absorption bands at 3400-3010 cm^{-1}, 2600-3000 cm^{-1}, 1500-1740 cm^{-1} and 1000-1200 cm^{-1}. The band found at 3338 cm^{-1} is assigned to the presence of OH O-H stretching vibration, while the band at around 2914 cm^{-1} is probably due to alkyl C-H stretches [23]. The strong band around 1735 cm^{-1} found in the raw sample shows the presence of stretching vibration of C=O bonds in ketones, aldehyde, lactone, and carboxyl [24].

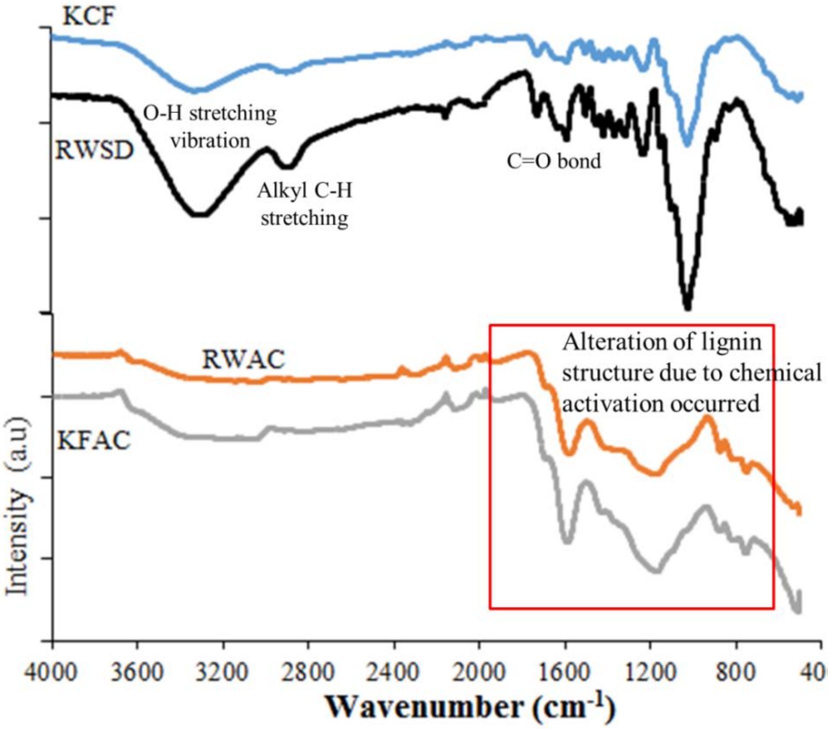

Fig. 4 FTIR spectra for KCF and RWSD

The functional groups that exist on the surface of the powdered activated carbons (KFAC and RWAC) are similar up to a certain extent. The bands of the KFAC and RWAC are different from their parent materials as numbers of bands disappeared due to carbonization and activation processes. Elimination of peaks at 2907 cm^{-1}, 1737 cm^{-1}, 1423 cm^{-1} and 1325 cm^{-1} from raw KCF and peaks at 2914 cm^{-1}, 1735 cm^{-1}, 1422 cm^{-1} and 1369 cm^{-1} from raw RWSD indicated on the disintegration of functional groups present in oxygenated hydrocarbons, portraying the carbohydrate structure of cellulose and hemicellulose [25]. The band intensity reduced from 1235 cm^{-1} of KCF and 1233 cm^{-1} of RWSD to 1218 cm^{-1} and 1222 cm^{-1} respectively after chemical activation. The reduction could be explained by alteration of lignin structure comprises of ester and ether linkage [24]. There were significant changes in the absorption band of raw material compared with AC product but the spectra showed that the surface functional groups of the AC do not exhibit significant differences, independently of the raw material used. Only slight differences in the intensity of the bands were detected due to the different chemical composition of the polymeric structure of cellulose, hemicellulose, and lignin [25].

Adsorption experiment

Effect of contact time

The study on the effect of contact time (0-180 min) using RWAC and KFAC was shown in Fig. 5. The activated carbons displayed a significant percentage removal of Al(III) and Cu(II) in the first 30 minutes and gradually reaching a steady trend line with a further increase in time. As for RWAC, the equilibrium was achieved at 120 min for both Al(III) and Cu(II) cations. The percentage of maximum adsorption was 69.0% for Al(III) and 53% for Cu(II). A study on the effect of contact time using KFAC has shown that the equilibrium for KFAC was achieved at 90 min for both Al(III) and Cu(II) cations. The highest percentage of adsorption obtained was 64.0% for Al(III) and 55% for Cu(II).

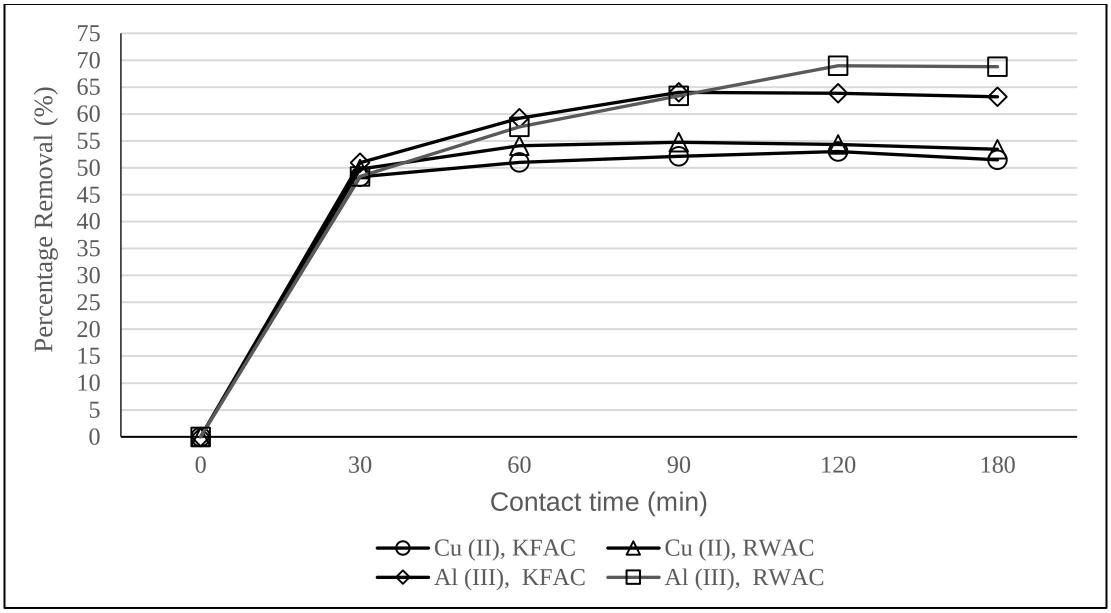

Fig. 5 Effect of contact time on the percentage removal of Al(III) and Cu(II) using RWAC and KFAC

The adsorption was rapid in the early stages as the adsorptive sites were highly available. The adsorption capacity at equilibrium for both adsorbents favored Al(III) than Cu(II). That indicated the affinity of acidic groups adsorbed onto RWAC and KFAC. The result could be explained by the charge density of cations ($Al^{+3} > Cu^{+2}$) and the diameter of the adsorbate ions which displayed better adsorption on Al(III) compared to Cu(II). The ionic radius of Cu(II) has 73 pm while Al(III) with 53 pm ionic radius obtained higher removal. This justified faster equilibrium achieved for Al(III) than Cu(II) ions [26] for RWAC and KFAC.

Effect of adsorbent dosage

The adsorbent dosage was varied from 0.4 g to 2.0 g and the percentage removals were higher as the adsorbent dosage increase for both RWAC and KFAC which showed in Fig. 6.

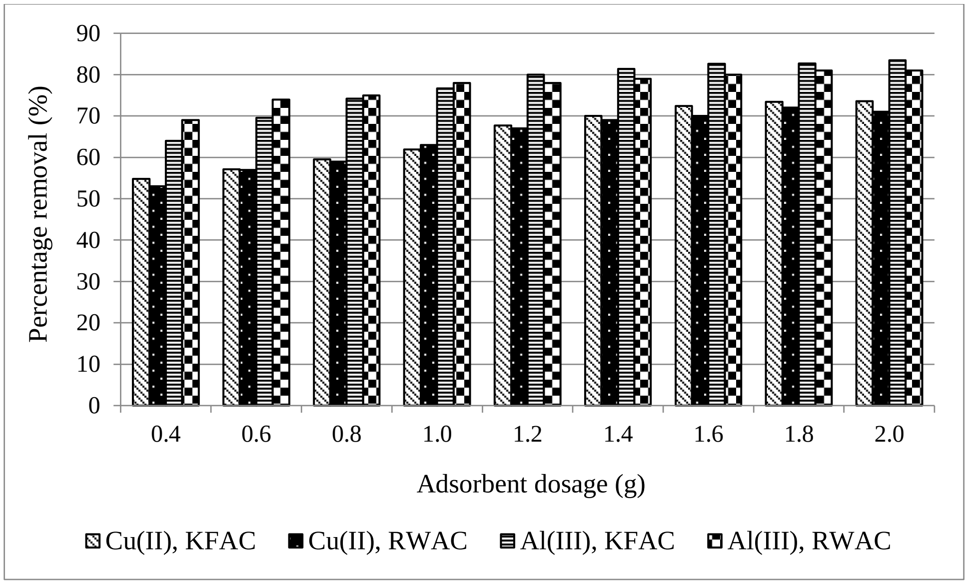

Fig. 6 Effect of adsorbent dosage on the percentage removal of Al(III) and Cu(II) using RWAC and KFAC

At an initial dose of 0.4 g, KFAC has shown 54.8% and 64.0% removal percentage for Cu(II) and Al(III), respectively. The percentage removal proceeded to 73.6% and 83.5 % for Cu(II) and Al(III)when the adsorbent amount of KFAC used was 2.0 g. RWAC also showed a similar increasing trend and this was supported by Sabela *et al.*, [27]. This finding can be justified by the fact that higher adsorbent dosage provides more available sites to the adsorbate molecules, consequently improved the adsorbent potential in the removal process. Therefore, the higher adsorbent dosage has a positive effect on the removal percentage of the metal ion.

Effect of pH

The effect of pH on the removal of Cu(II) and Al(III) was studied on the selected pH of 3, 5, 7, 9, 11. The percentage removal using RWAC and KFAC was shown in Fig. 7, respectively. The best percentage of removal was observed at neutral pH with maximum Al(III) removal percentage was 85.77% and 88.96% for RWAC and KFAC, respectively. However, Cu(II) removal using KFAC was 86.8% in acidic conditions (pH 3). Although Cu(II) seems favored acidic solution to work best within this study, a previous study by Sabela *et al.*, [27] and Bouhamed *et al.*, [28] claimed that Cu(II) removal enhanced with increasing pH condition as at lower pH has a higher number of hydronium ion which could be competing against active sites that bind with targeted copper ion, thus lowering the adsorption capacity effectiveness [27-28]. However, in alkaline conditions (pH 11), the removal of Cu(II) was very least where 74% and 72.8% of removal percentage was obtained when KFAC and RWAC were used, respectively. This happened due to the precipitation of copper hydroxide in the solution [27].

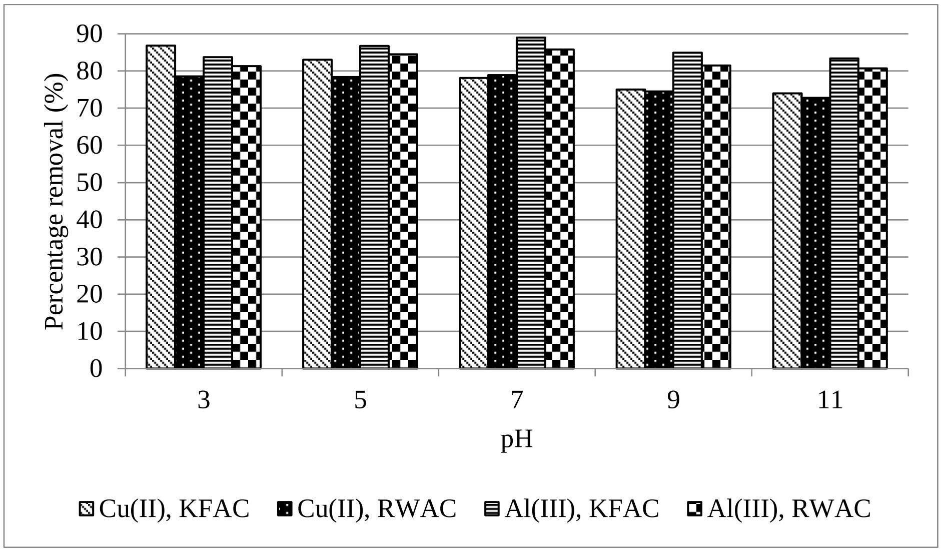

Fig. 7 Effect of pH value on the percentage removal of Al(III) and Cu(II) using RWAC and KFAC.

Conclusion

The activated carbon from RWAC and KFAC were potential in removing Al(III) and Cu(II) ions from textile wastewater where removal of heavy metal by both activated carbon nearly reached 50% within 30 minutes of contact time. Clear FESEM image on the pore development after carbonization and acid treatment indicated the suitability of the raw material used. It can be concluded that either KFAC or RWAC, both were contributed to the higher percentage removal of heavy metal once higher dosage of activated carbon was applied. Whereas, Al(III) was best removed at neutral pH and Cu(II) at pH 3when KFAC was used.

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Author Contributions

All authors contributed toward data analysis, drafting, and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

References

[1] Pirkarami, A. & Olya, M. E. (2014) Removal of Dye from Industrial Wastewater with an Emphasis on Improving Economic Efficiency and Degradation Mechanism. *J. Saudi Chem. Soc.* 21(1) 179-186.

[2] Sharma, P., Singh, L. & Mehta, J. (2010) Cod Reduction and Colour Removal of Simulated Textile Mill Wastewater by Mixed Bacterial Consortium. *Rasayan J. Chem.* 3(4) 731–735.

[3] Mohamad Thani, N.S., Mohd Ghazi, R., Mohd Amin, M.F. & Hamzah, Z. (2019) Phytoremediaton of Heavy Metals from Wastewater by Constructed Wetland Microcosm Planted with *Alocasia puber, J. Teknol*. 81, 17-23.

[4] Mohamad Thani, N.S., Mohd Ghazi, R., Abdul Wahab, I.R., Mohd Amin, M.F., Hamzah, Z. & Nik Yusoff, N.R. (2020) Optimization ofPphytoremediation of nickel by *Alocasia puber* using Response Surface Methodology, *Water* 12, 1-16.

[5] Azmi, A.A., Ahyat, N.M., Mohamad, F., & Hamzah, S. (2020) Synthesis of Silver Nanoparticles: Double-green Approach of using Chitosan and Microwave Techniques Towards Antimicrobial Activity Against Pathogenic Bacteria, *Biointerface Res. Appl. Chem.* 10, 5918-5922.

[6] Azmi, A.A. & Ahyat, N.M. (2015) Green Synthesis of Silver Nanoparticles using Rhizome Extract of Galangal, *Alpinia galangal*, *Malaysian J. Anal. Sci*. 19, 1187-1193.

[7] Bhat, I.U.H., Anwar, M.N.K., Nik Yusoff, N.R. & Eh Rak, A. (2018) Palladium Catalyst for Treatment of Inorganic and Organic Pollutants in Wastewater: A short review, *Desalin. Water Treat.* 131, 132-140.

[8] Liu, F., Zhang, G. L., Meng, Q. & Zhang, H.Z. (2008) Performance of Nanofiltration and Reverse Osmosis Membranes in Metal Effluent Treatment. *Chin. J. Chem. Eng.* 16(3) 441–445.

[9] Hogland, W. & Marques, M. (2016) An Overview of the Modification Methods of Activated Carbon for its Treatment Applications. *Chem. Eng. J.* 219, 499-511.

[10] Gopalakrishnan, K. & Jeyadoss, T. (2011) Comparative Study on Biosorption of Zn(II), Cu(II) and Cr(VI) from Textile Dye Effluent using Activated Rice Husk and Activated Coconut Fiber. *Indian J. Chem. Technol.*18(1) 61–66.

[11] Maizatul, N.N., Ghazali, M.F. & Nik Yusoff, N.R (2020) Removal of Cu from Printed Circuit Board (PCBs) Leachates using Activated Carbon derived from Foxtail Palm Fruit. *IOP Conf. Ser.:Earth Environ. Sci.* 549(1) 012057.

[12] Mohd Alias, M.Z., Mohd Ghazi, R., Nik Yusoff, N.R. & Jamaludin, M.H. (2020) The Efficiency of Bamboo Activated Carbon for Removal of COD from Fish Cracker Industry Wastewater via Response Surface Methodology (RSM), *IOP Conf. Ser.: Earth Environ. Sci.* 549(1) 012058.

[13] Subki, N.S., Akhir, N.M. Abdul Halim, N.S. & Nik Yusoff, N.R (2020) Cod Reduction in Industrial Wastewater using Activated Carbon derived from Wodyetia Bifurcata Fruit. *IOP Conf. Ser.:Earth Environ. Sci.* 549(1) 012066.

[14] APHA (1998). *Standard Methods for the Examination of Water and Wastewater*. 20th edition (American Public Health Association, American Water Works Association and Water Environmental Federation, Washington DC).

[15] Sulaiman, M.A., Shamsuddin, M.S. & Nik Yusoff, N.R (2016) Synthesis and Characterization of Activated Carbon Produced from *Kenaf* core fiber using H_3PO_4 Activation. *Procedia Chem.* 19: 558-565.

[16] Kumar, A. & Jena, H.M. (2016) Preparation and Characterization of High Surface Area Activtaed Carbon from Fox Nut (*Euryale ferox*) shell by Chemical Activation. *Result Phys.*6: 651-658.

[17] Al-Swaidan H. & Ahmad A. (2011) Synthesis And Characterization Of Activated Carbon From Saudi Arabian Dates Trees Fronds Wastes. In *3rd International Conference on Chemical, Biological and Environmental Engineering IPCBEE* Vol 20, pp. 25-31.

[18] Chowdhury, Z. Z., Zain, S. M., Khan, R. A., Ahmad, A. A., & Islam, M. S. (2011) Application of Central Composite Design for Preparation of Kenaf Fibre Based Activated Carbon for Adsorption of Manganese(II) Ion. *Int. J. Phys. Sci.* 6(31) 7191-7202.

[19] Thanapal, S. S., Chen, W., Annamalai, K., Carlin, N., Ansley, R. J., & Ranjan, D. (2014) Carbon Dioxide Torrefaction of Woody Biomass. *Energ. Fuels* 28(2) 1147–1157.

[20] Hong, B., Xue, G., Weng, L., & Guo, X. (2012) Pretreatment of Moso Bamboo with Dilute Phosphoric Acid. *BioResources* 7(4) 4902–4913.

[21] Shrestha R.M., Yadav A.P., Pokharel B.P. & Pradhananga R.P. (2012) Preparation and Characterization of Activated Carbon from Lapsi (*Choerospondias axillaris*) Seed Stone by Chemical Activation with Phosphoric Acid. *Res. J. Chem. Sci.* 2(10) 80–86.

[22] Yakout, S. M., & El-deen, G. S. (2012) Characterization of Activated Carbon Prepared by Phosphoric Acid Activation of Olive Stones. *Arab. J. Chem.* 9(2) S1155-S1162.

[23] Azlina, W., Abdul, W., Ghani, K., Mohd, A., Bachmann, R. T., Taufiq-yap, Y. H. & Al-Muhtaseb, A. H. (2013) Biochar Production from Waste Rubber-Wood-Sawdust and Its Potential Use in Carbon Sequestration : Chemical and Physical Characterization. *Ind. Crops Prod.* 44, 18–24.

[24] Kenneth A., Casimir E.G., Agbaji E. & Stephen A.E. (2015) Structural and Microstructural Properties of Neem Husk and Seed Carbon Activated with Zinc Chloride and Phosphoric Acid. *J. Chem. Pharm. Res.* 7(3) 2470–2479.

[25] Jiang, D., Tianyi, X., Haiyan, W. & Anmin, Z. (2016) Effect of Cellulose, Hemicellulose and Lignin on the Structure and Morphology of Porous Carbons. *ACS Sustainable Chem. Eng.* 4(7) 3750–3756.

[26] Nebagha, K. C, Khadija, Z., Lotfi, R., Mohamed, K., Mohamed, S., Khadija, A., Abderrahim, E. H. & Said, S. (2015) Adsorptive Removal of Copper(II) from Aqueous Solution using Low Cost Moroccon Adsorbent Part I: Parameters Influencing Cu(II) Adsorption. *J. Mater. Environ. Sci.* 6(11) 3022-3033.

[27] Sabela, I.M., Kunene, K., Kanchi, S., Xhakaza, M.N., Bathinapatla, A., Mdluli, P., Sharma, D. & Bisetty, K. (2016) Removal of Copper (II) from Wastewater using Green Vegetable Waste Derived Activated Carbon: An Approach to Equilibrium and Kinetic Study. *Arab. J. Chem.* 12(8) 4331-4339.

[28] Bouhamed F., Elouear Z. & Bouzid J. (2012). Adsorptive Removal of Copper (II) from Aqueous Solutions on Activated Carbon Prepared from Tunisian Date Stone: Equilibrium, Kinetics and Thermodynamics. *J. Taiwan Inst. Chem. E.* 43(5) 741-749.