



Research Article

Evaluation of Low Cost-Activated Carbon Produced from Waste Tyres Pyrolysis for Removal of 2-Chlorophenol

Kanchana Manirajah, Sheela V. Sukumaran, Nornasuha Abdullah, Hazirah A. Razak, Nurul Ainirazali*

Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

Received: 15th November 2018; Revised: 7th February 2019; Accepted: 8th February 2019; Available online: 30th April 2019; Published regularly: 1st August 2019

Abstract

A low cost Activated Carbon (AC) was prepared by using waste tyres as raw material for the removal of 2-chlorophenol (2-CP). The AC adsorbent was prepared and activated by pyrolysis process at 900 °C under constant nitrogen flow. The physical properties of the AC produced was characterized using X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET), Field Emission Scanning Electron Microscopy (FESEM), and Fourier Transform Infra Red (FTIR). The influence of initial adsorbate concentration, pH and adsorbent dosage on the removal of 2-CP in the batch-operational mode at ambient temperature were also investigated. The results obtained showed the AC presence of an amorphous carbon with high BET surface area and a total pore volume of 208 m².g⁻¹ and 0.5817 cm³, respectively. The highest adsorption capacity of 2-CP by the AC adsorbent was achieved at an initial concentration of 10 mg.L⁻¹, pH 5, and adsorbent dosage of 0.5 g in the first 10 min of contact time. This finding proves that the low cost-AC produced from waste tyres can be utilized for an effective removal of chemical plant wastewater containing toxic chlorine substances. Copyright © 2019 BCREC Group. All rights reserved

Keywords: Waste tyre; Activated Carbon; Adsorption; 2-Chlorophenol; Pyrolysis

How to Cite: Manirajah, K., Sukumaran, S.V., Abdullah, N., Razak, H.A., Ainirazali, N. (2019). Evaluation of Low Cost-Activated Carbon Produced from Waste Tyres Pyrolysis for Removal of 2-Chlorophenol. *Bulletin of Chemical Reaction Engineering & Catalysis*, 14(2): 443-449 (doi:10.9767/bcrec.14.2.3617.443-449)

Permalink/DOI: <https://doi.org/10.9767/bcrec.14.2.3617.443-449>

1. Introduction

Most phenolic compounds including 2-chlorophenol (2-CP) are categorized as a major pollutant to human being due to its high toxicity even at low concentration [1]. The 2-CP has also been categorized as an aquatic pollutant as its has been discovered that it is being released to the surrounding via anthropogenic activities.

Continuous discharge of 2-CP will ultimately have a negative impact to the aquatic ecosystem [2]. Humans who were exposed to high concentration of 2-CP developed adverse effects, such as: dizziness, loss of nervous system, decrease in capability, difficult in focusing, and irregular heartbeat [2,3]. Therefore, it is necessary to treat the wastewater containing phenolic compounds before its being released to the river and environment.

Various process, such as: adsorption [4] catalytic wet oxidation [5], biodegradation [6], ozonation, and electrochemical degradation [7], have been studied regarding treatment of waste

* Corresponding Author.

E-mail: ainirazali@ump.edu.my (N. Ainirazali);
Telp: +60-9-5492833, Fax: +60-9-5492889

water containing chlorophenol. Among all the studied process, adsorption technology for treatment of chlorophenol was well-agreed as the most significant technique. This is due to the fact that properties and types of material that were being used as adsorbent plays a crucial role to achieve high chlorophenol removal.

AC was commonly produced by pyrolysis process and is widely used for industrial scale as an adsorbent especially for purification or separation of liquid and gases [4,8,9]. AC also has been proven to be an effective adsorbent mainly for organic and inorganic compounds due to its large surface area of $3000 \text{ m}^2 \cdot \text{g}^{-1}$, defined porosity, and its unique chemical properties [10]. The porous structure of AC provides a network of interconnected macropores, mesopores, micropores that enhances the capacity for the adsorption of the organic molecules. However, commercial AC requires high production costs which tends to be more expensive compare to other adsorbent. Therefore, materials rich in carbon content, such as: tyres, which can be found abundantly as waste materials can be used as an alternative source to produce AC. This can be considered as a green approach, since it can reduce the cost of raw material, eliminate fire hazard and addresses solution related to the disposal of pollutant waste tyres [10,11]. In this contribution, problematic waste tyre was used as raw material in producing AC adsorbent for treatment of chlorine compound, focusing on the effects of process conditions on removal of 2-chlorophenol.

2. Materials and Methods

2.1 Materials

Pure 2-chlorophenol (2-CP), hydrogen peroxide (H_2O_2), potassium hydroxide (KOH) and hydrochloric acid (HCl), purchased from Sigma-Aldrich. Waste tyre used in this study was taken from BS tyre shop located in Gambang, Pahang.

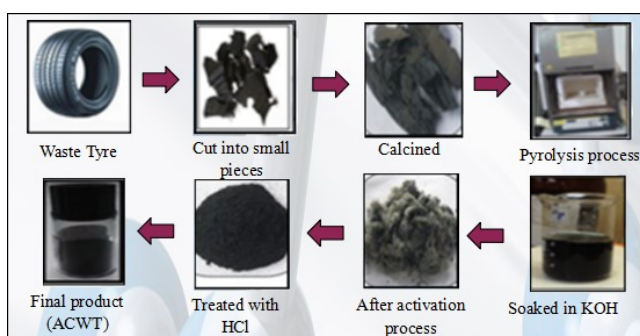


Figure 1. Schematic diagram for preparation of AC

2.2 Preparation of AC Adsorbent from Waste Tyre

Initially, the cleaned waste rubber tyre was cut to small granulates before being dried at $110 \text{ }^\circ\text{C}$ for 2 h. The granules were then heated up to $300 \text{ }^\circ\text{C}$ in furnace for 3 h in order to produce black tire crude oil and distilled diesel oil. Next, the activations of char was done by placing it at into the pyrolysis reactor at $500 \text{ }^\circ\text{C}$ for 5 h with constant nitrogen flow of 200 mL min^{-1} . The chars were then recovered from the pyrolysis reactor and was treated with hydrogen peroxide, H_2O_2 (6% concentration) with carbon/ H_2O_2 ratio of $1 \text{ g } 20 \text{ mL}^{-1}$. The mixture was then placed in an oven and heated at $100 \text{ }^\circ\text{C}$ for 24 h. The obtained sample was then washed thoroughly with deionized water and dried at $110 \text{ }^\circ\text{C}$ for 2h to form activated carbon. Next, the activated carbon was soaked with KOH at $30 \text{ }^\circ\text{C}$ for 30 min with a weight ratio of 1:3 and then dried in oven at $60 \text{ }^\circ\text{C}$ for 2h. The activations were taken place at an activation temperature of $900 \text{ }^\circ\text{C}$ in the presence of $200 \text{ mL} \cdot \text{min}^{-1}$ nitrogen gas for 3 h. Further modification of rubber tyre carbon in creating oxygen surface groups was done by acid treatment of 37 M HCl. The mixture of carbon and acid solution was stirred and heated at $100 \text{ }^\circ\text{C}$ for 24 h. The resulted sample was then washed and dried at $100 \text{ }^\circ\text{C}$ until a black powder was formed.

2.3 Characterization of AC Adsorbent

The physical and chemical properties of the produced AC were characterized using XRD, BET, FESEM, and FTIR. The crystalline structure of the AC was evaluated by X-ray diffraction (XRD) in the range of 2θ of $10 - 80^\circ$ with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5405\text{\AA}$). The specific surface area, pore volume, and pore diameter of AC were measured at 77 K using AUTOSORB-1 model AS1 MP-LP instrument. The surface morphology of the AC was viewed by field emission scanning electron microscope (FESEM), JEOL/JSM-7800F with accelerating voltage employed to be in the range of 5-15 kV. The IR spectra of the AC adsorbent was measured on Perkin-Elmer System 2000 spectrometer using the KBr disk method over the range of $2000-400 \text{ cm}^{-1}$.

2.4 Batch Adsorption Study of 2-Chlorophenol

The equilibrium adsorption was studied by using batch mode adsorption. A constant mass of adsorbent of 0.1 g was contacted with 50 mL of 2-CP solutions of $10 \text{ mg} \cdot \text{L}^{-1}$. The flasks were then sealed properly and placed in an incuba-

tion shaker for further adsorption process. Samples were taken every 5 min until an equilibrium reaction was achieved, in which at this condition, the removal of 2-chlorophenol was complete. The sample was filtered through 0.22 m syringe filter and diluted to the desired concentration for analysis. Similar adsorption procedure was repeated by varying the initial pH of 2-CP solution (3, 5, 7, and 10) and adsorbent dosage (0.05, 0.1, 0.3, and 0.5) g.

2.5 Analysis of 2-Chlorophenol

The removal of 2-CP was analysed using Varian Cary 1E UV-Vis spectrophotometer, in which the wavelength of 2-CP is 284 nm. The percentage removals (%R) of 2-chlorophenol by AC adsorbent was calculated using Equation (1).

$$CP_S \text{ removal} = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

where C_o and C_e are the concentrations of liquid-phase at initial and equilibrium states ($\text{mg}\cdot\text{L}^{-1}$), respectively. The equilibrium amount of CPs adsorbed per unit mass of adsorbent, q_e ($\text{mg}\cdot\text{g}^{-1}$), at different 2-CP concentrations was identified using Equation (2)

$$q_e = \frac{(C_o - C_e)V(l)}{W(g)} \quad (2)$$

where q_e ($\text{mg}\cdot\text{g}^{-1}$) is the adsorbate equilibrium amount (CPs) per unit mass of adsorbent (AC); V is the volume of the solution (liter) and W is the mass of the adsorbent (gram).

3. Results and Discussion

3.1 Characterization of AC

Figure 2 shows the XRD pattern for the AC adsorbent produced from waste tyre. The result indicates the presence of two peaks at 2θ of 25.43 and 43.89°. The peaks pattern indicates the presence of an amorphous carbon caused by disordered stacked of carbon ring [12].

Table 1. Properties of AC

Parameters	Value
BET surface area ($\text{m}^2\cdot\text{g}^{-1}$)	208
Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	0.5817
Average pore diameter (Å)	126
Mesopore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	0.5611
Micropore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	0.0206

The isotherms produced by AC showed in Figure 3 was corresponding to type IV adsorption characteristics [4,12]. Table 1 summarizes the properties of AC produced from waste tyre. The results show the adsorbent possessed a high surface area of $208 \text{ m}^2\cdot\text{g}^{-1}$ and total pore volume of $0.5817 \text{ cm}^3\cdot\text{g}^{-1}$ with most of the pores in the meso-range. These positive results were most probably due to the activation temperature of $900 \text{ }^\circ\text{C}$ that were used during pyrolysis process. At $900 \text{ }^\circ\text{C}$, more energy is being supplied for the reaction of steam-carbon, which would create new pores and enhance the enlargement of existing pores. This situation leads to the development of more mesopores rather than micropores. Pejman *et al.* [13] reported that different surface area of activated carbon was correlated with the lower temperature

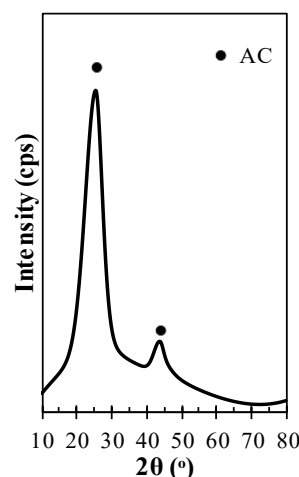


Figure 2. XRD analysis of AC

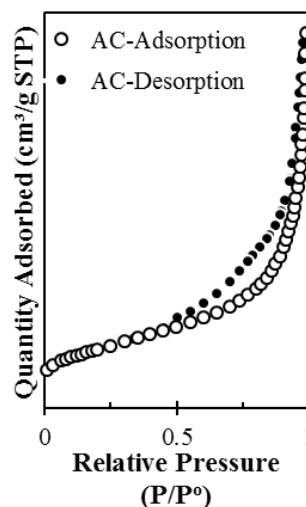


Figure 3. N_2 adsorption-desorption isotherm for AC

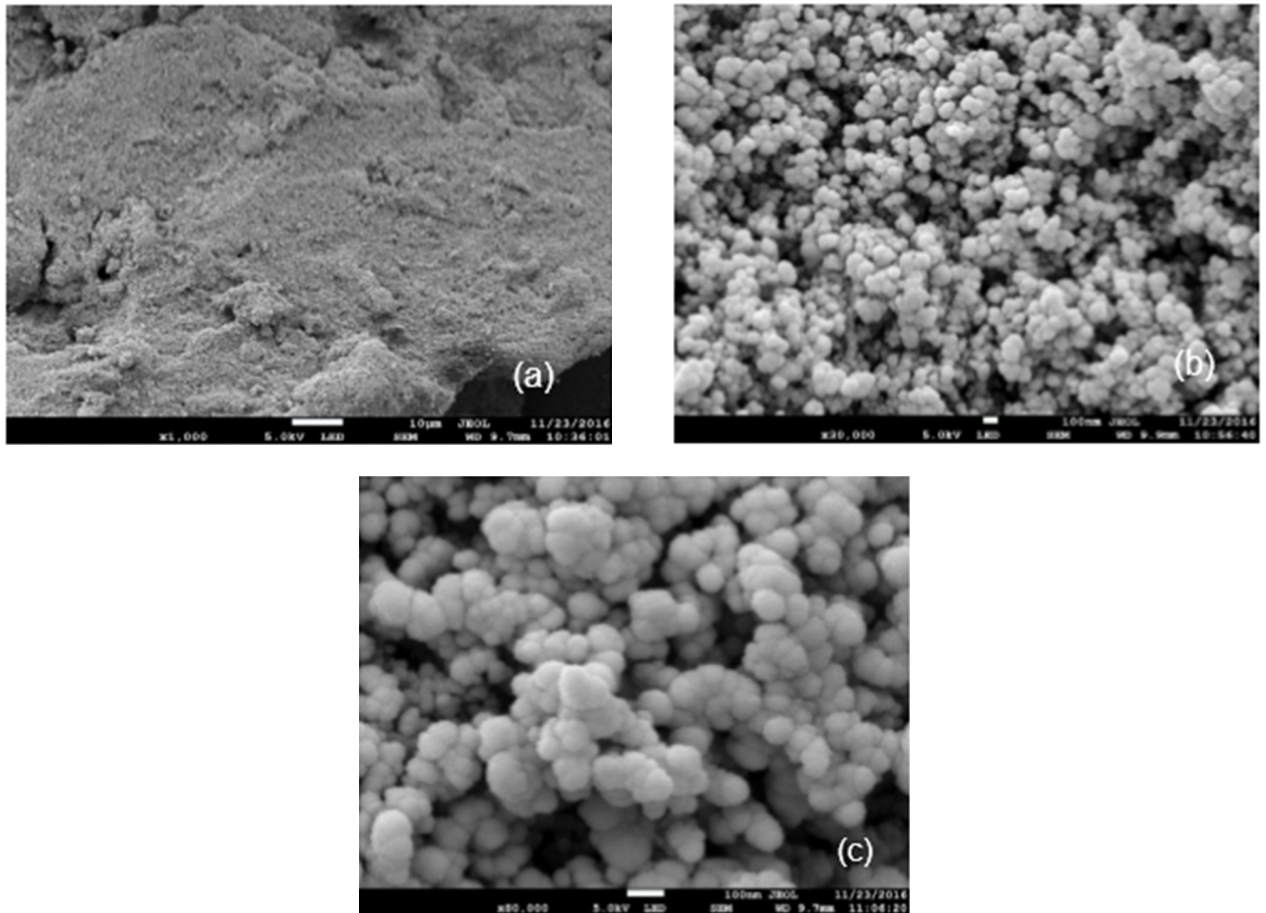


Figure 4. FESEM images of AC, under magnification (a) 1000x, (b) 30000x, and (c) 80000x

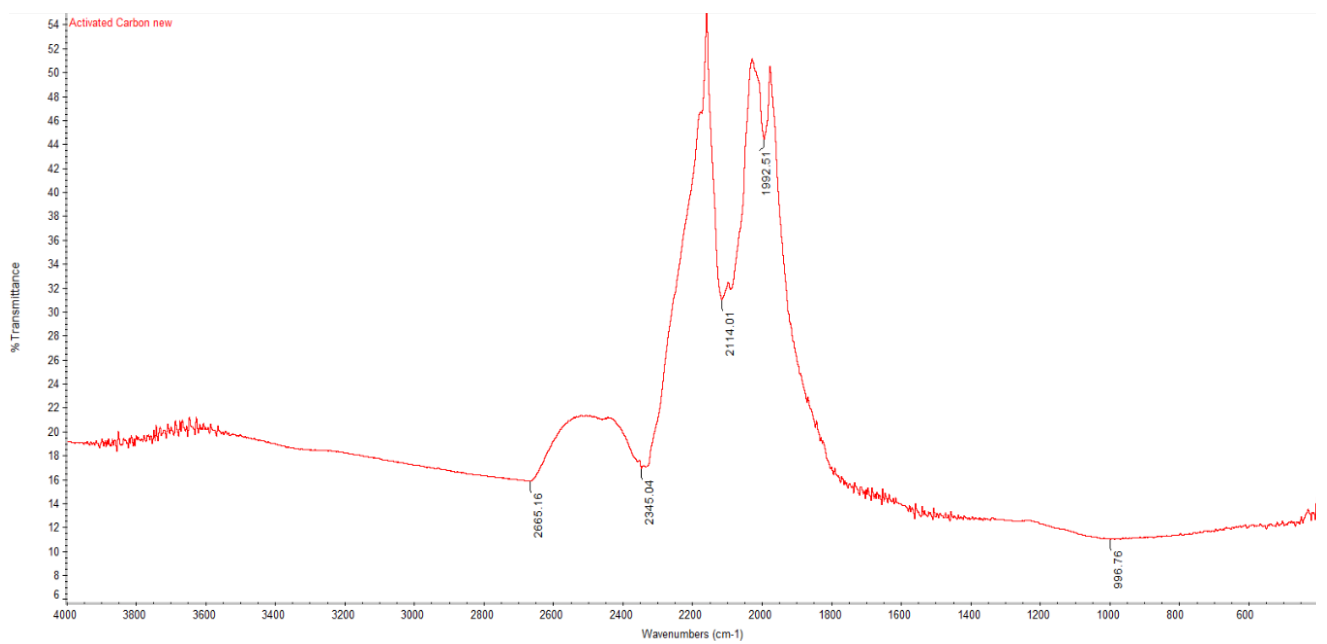


Figure 5. FTIR spectrum of the AC

of pyrolysis. Pyrolysis temperature lower than 900 °C tends to produce carbonaceous materials with lower surface area (<70 m².g⁻¹) and total pore volume of 0.20 cm³.g⁻¹ [13,14]. High surface area of AC produced from waste tyre is believed to act as an efficient adsorbent for treatment of pollutant in waste water as its can increase the adsorption capacity.

The surface morphology of the produced AC was shown in Figure 4. The result displays the porous structure of AC with granular morphology. Figure 3 (b) clearly shows the uniform size of the morphology which was formed by agglomeration of AC particles. This morphology might lead to a high surface area and pore volume of the material.

FTIR spectroscopy is an analytical tool for qualitatively determine the chemical changes and functional group of the adsorbent, and the common wavelength present in AC associate to specific functional group is summarized in Table 2.

Table 2. Functional group according to wave-number [15-17]

Wavenumber (cm ⁻¹)	Functional Group
1030 – 1155	C–O
1550 – 1650	NH ₂
600 – 400	Aromatic ring
2500 – 3500	O–H
2880 – 2500	C–H
3300 – 3500	N–H

Figure 5 shows the FTIR spectra of synthesized AC from waste tyre. A wide transmittance band was observed at 3200-3600 cm⁻¹ with a maximum band at 3440 cm⁻¹ [15]. This band can be attributed to the O–H stretching vibration which was due to the surface of hydroxyl groups and chemisorbed water. The peaks at 2345 cm⁻¹ and 2665 cm⁻¹ indicate the strong bonded functional group of O–H and C–H stretching absorption, respectively. The band centered on 1992 cm⁻¹ indicates the presence of aromatic C=C groups (carbonization), which proved the presence of carbonization processes during the AC synthesis. While, the peak at 997 cm⁻¹ represents C–O stretching functional group [16,17]. Fingerprint region occurs towards the end. Fingerprint region is the region consists of absorptions due to all other single bonds (except H-Z), making it often a complex region that is very difficult to analyze.

3.2 Adsorption Study on AC

3.2.1 Effect of initial 2-CP concentration

The effect of different initial concentration of 2-CP on the adsorption capacity of AC is illustrated in Figure 6. The highest adsorption performance was achieved at 10 ppm (mg.L⁻¹) with 0.1 g of adsorbent dosage. The adsorption process of chlorinated hydrocarbons was rapidly increased at initial time of 10 min due to high availability of vacant active sites with large specific surface area and total pore volume of AC. However, the adsorption rate reduced after 10 min until an equilibrium state was achieved. This was correlated with the slower internal diffusion process as the repulsive forces of solute molecules with AC surfaces

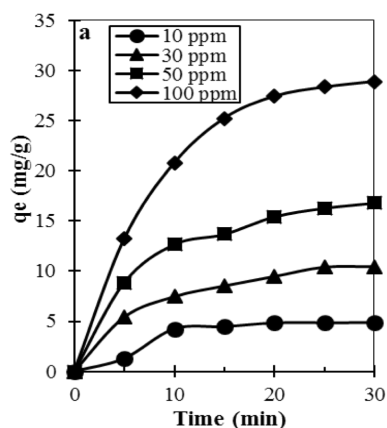


Figure 6. Effect of contact time on adsorption at different initial concentrations

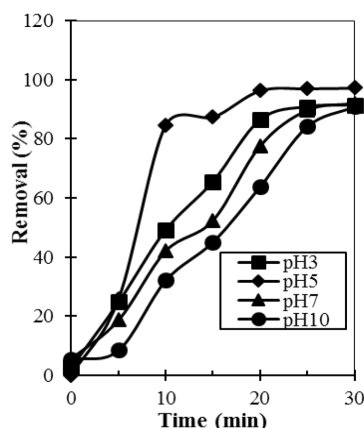


Figure 7. Effect of pH on removal 2-CP

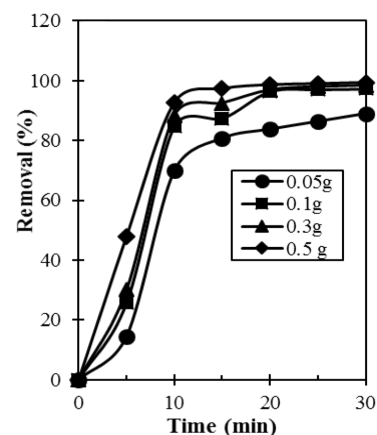


Figure 8. Effect of adsorbent dosage on removal of 2-CP

in bulk phases became slower [18,19]. Thus, longer contact time is required to reach the equilibrium when high initial concentration was treated. The Langmuir constant, K_L for Figure 6 was determined using Langmuir equation: $Ce/q_e = 1/q_m K_L + Ce/q_m$, and the value is 0.067 L/mg.

3.2.2 Effect of pH

Figure 7 indicates the influences of pH 3-10 on adsorption of 2-CP. It is well known that 2-CP is a weak acid, and removal of 2-CP was associated with the chlorine detached from the phenol aromatic ring [20,21]. The AC removal efficiency towards 2-CP showed a positive behaviour in acidic condition at pH 3 and 5 compared to neutral (pH 7) and alkali condition (pH 10). This was due to the presence of acidic solute molecules in the solution. The location of AC in acidic solution (pH < 6) makes the outer surface of AC being surrounded with H_3O^+ positive charge. In this study, 100% removal of 2-CP by AC were achieved at pH 5 in 30 min. This is due to the presence of H_3O^+ on AC surfaces that act as active adsorption sites to interact with 2-CP molecule. This eventually led to the increase of adsorption capacity which then favoured the removal of 2-CP. While, in basic solution of pH 10, the surface of AC richest with negative charges of OH^- was not effectively reacting with the partial negative charge of 2-CP. This resulted in the decrease in adsorption capacity of 2-CP on AC adsorbent.

3.2.3 Effect of AC Adsorbent Dosage

The effect of AC dosage from 0.05 to 0.5 g towards removal of 2-CP were shown in Figure 8. At reaction temperature of 25 °C, initial concentration showed 10 mg.L⁻¹ within 30 min of reaction time, the percent removal of 2-CP increased as the adsorbent dosage increased. This was related to the high availability of adsorption active sites when more AC was introduced as adsorbent dosage. Therefore, dosage amount is directly proportional to the adsorption capacity.

4. Conclusion

The AC produced from waste tyre in this research work demonstrated the effective performance on removal of chlorine substance from 2-CP. This was associated with its high surface area (208 m².g⁻¹) and total pore volume (0.5817 cm³ g⁻¹), which was favorable for interaction of chlorine with the AC active sites during adsorption process. Adsorption studies showed

the rapid chlorine adsorption with almost 100% removal over 0.5 g AC was achieved at initial 2-Cp concentration 10 ppm and pH 5 within 10 min of contact time.

Acknowledgments

The authors express their gratitude to the Universiti Malaysia Pahang for the support under the internal research grant (RDU170330 and RDU1803184).

References

- [1] Yagub, M.T., Sen, T.K., Afroze, S., Ang, H.M. (2014). Dye and its removal from aqueous solution by adsorption: A review. *Adv. Colloid Interface Sci.*, 209: 172–184.
- [2] Foo, K.Y. (2018). Effect of microwave regeneration on the textural network, surface chemistry and adsorptive property of the agricultural waste based activated carbons. *Process Saf. Environ. Prot.*, 116: 461–467.
- [3] Jardines, M.M., Hernandez, S.M., Texier, A.C., Lopez, F.C. (2018). 2-Chlorophenol consumption by cometabolism in nitrifying SBR Reactors. *Chemosphere* 212: 41-49
- [4] Soltani, T., Lee, B.K. (2016). Mechanism of highly efficient adsorption of 2-chlorophenol onto ultrasonic graphene materials: Comparison and equilibrium. *J. Colloid Interface Sci.*, 481: 168–180.
- [5] Chaliha, S., Bhattacharyya, K.G. (2008). Catalytic wet oxidation of 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol in water with Mn(II)-MCM41. *Chem. Eng. J.*, 139: 575–588.
- [6] Dobaradaran, S., Nodehi, R.N., Yaghmaeian, K., Jaafari, J., Niari, M.H., Bharti, A.K., Agarwal, S., Gupta, V.K., Azari, A., Shariatifar, N. (2018). Catalytic decomposition of 2-chlorophenol using an ultrasonic-assisted Fe₃O₄-TiO₂@MWCNT system: Influence factors, pathway and mechanism study. *J. Colloid Interface Sci.*, 512: 172–189.
- [7] Lim, J.W., Lim, P.E., Seng, C.E., Adnan, R. (2013) Simultaneous 4-chlorophenol and nitrogen removal in moving bed sequencing batch reactors packed with polyurethane foam cubes of various sizes. *Bioresour. Technol.*, 129: 485–494.
- [8] Gupta, N., Kushwaha, A.K., Chattopadhyaya, M.C. (2012). Adsorption studies of cationic dyes onto Ashoka (*Saraca asoca*) leaf powder. *J. Taiwan Inst. Chem. Eng.*, 43: 604–613.
- [9] Blanco, P.H., Wu, C., Williams, P.T. (2014). ScienceDirect Influence of Ni/SiO₂ catalyst preparation methods on hydrogen production from the pyrolysis / reforming of refuse de-

- rived fuel. *Int. J. Hydrogen Energy*. 39: 5723-5732.
- [10] Allaboun, H., Abu, Al-Rub, F.A. (2016). Removal of 4-chlorophenol from contaminated water using activated carbon from dried date pits: Equilibrium, kinetics, and thermodynamics analyses. *Materials (Basel)*, 9: 166-180.
- [11] Al-Rahbi, A.S., Williams, P.T. (2016). Production of activated carbons from waste tyres for lowfile: *Waste Manag.*, 49: 188-195.
- [12] Ganiyu, S.A., Alhooshani, K., Sulaiman, K.O., Qamaruddin, M., Bakare, I.A., Tanimu, A., Saleh, T.A. (2016). Influence of aluminium impregnation on activated carbon for enhanced desulfurization of DBT at ambient temperature: Role of surface acidity and textural properties. *Chem. Eng. J.*, 303: 489-500.
- [13] Pejman, H., Kit, Y.Y., Jiabin, G., Huaimin, W., Gordon, M.K. (2016). Sustainable development of tyre char-based activated carbons with different textural properties for value-added applications. *J. Env. Manag.*, 170: 1-7.
- [14] Abaide, E.R., Anchieta, C.G., Foletto, V.S., Reinehr, B., Nunes, L.F., Kuhn, R.C., Mazutti, M.A., Foletto, E.L., Abaide, E.R., Anchieta, C.G., Foletto, V.S., Reinehr, B., Nunes, L.F., Kuhn, R.C., Mazutti, M.A., Foletto, E.L. (2015). Production of Copper and Cobalt Aluminate Spinels and Their Application As Supports for Inulinase Immobilization. *Mater. Res.*, 18: 1062-1069.
- [15] Yakout, S.M., Sharaf, El-Deen. G. (2016). Characterization of activated carbon prepared by phosphoric acid activation of olive stones. *Arab. J. Chem.*, 9: S1155-S1162.
- [16] He, X., Wu, Z., Sun, Z., Wei, X., Wu, Z., Ge, X., Cravotto, G. (2018). A novel hybrid of β -cyclodextrin grafted onto activated carbon for rapid adsorption of naphthalene from aqueous solution. *J. Mol. Liq.*, 255:160-167.
- [17] Begum, S., Ahmaruzzaman, M. (2018). Green Synthesis of SnO₂ Nanoparticles loaded on Activated Carbon and its Application as Photocatalyst in the Degradation of Alizarin Red S Dye. *Mater. Today Proc.*, 5: 2314-2320.
- [18] Dil, E.A., Ghaedi, M., Asfaram, A., Hajati, S., Mehrabi, F., Goudarzi, A. (2017). Preparation of nanomaterials for the ultrasound-enhanced removal of Pb²⁺ ions and malachite green dye: Chemometric optimization and modeling. *Ultrason. Sonochem.* 34: 677-691
- [19] Gialamouidis, D., Mitrakas, M., Liakopoulou-Kyriakides, M. (2010). Equilibrium, thermodynamic and kinetic studies on biosorption of Mn(II) from aqueous solution by *Pseudomonas* sp., *Staphylococcus xylosus* and *Blakeslea trispora* cells. *J. Hazard. Mater.* 182: 672-680
- [20] Kudo, A., Omori, K., Kato, H. (1999). A novel aqueous process for preparation of crystal form-controlled and highly crystalline BiVO₄ powder from layered vanadates at room temperature and its photocatalytic and photophysical properties. *J. Am. Chem. Soc.*, 121: 11459-11467
- [21] Fulazzaky, M.A., Khamidun, M.H., Din, M.F.M., Yusoff, A.R.M. (2014). Adsorption of phosphate from domestic wastewater treatment plant effluent onto the laterites in a hydrodynamic column. *Chem. Eng. J.*, 258: 10-17.

Selected and Revised Papers from The 4th International Conference of Chemical Engineering & Industrial Biotechnology (ICCEIB 2018) (<http://icceib.ump.edu.my/index.php/en/>) (Universiti Malaysia Pahang, by 1st-2nd August 2018) after Peer-reviewed by Scientific Committee of ICCEIB 2018 and Peer-Reviewers of Bulletin of Chemical Reaction Engineering & Catalysis