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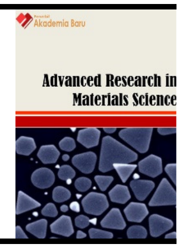

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Low-Cost Activated Carbon Produced from Waste for Removal of 2-Chlorophenol

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ABSTRACT

Waste tyre was used as a precursor for preparation of low-cost activated carbon ˚AC) as an adsorbent for removal of 2-chlorophenol ˚2-CP) from an aqueous solutions. The AC was produced by pyrolysis process. The physical and chemical properties of as-synthesized adsorbent were characterized by XRD, BET, FESEM, and 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 investigated. The as-synthesized AC presence an amorphous carbon with high surface area ˚208 m2/g) and average pore volume ˚0.5817 cm3/g) as revealed by XRD and BET. The maximum adsorption capacity for 2-CP by activated carbon was achieved at initial concentration 10mg/L, pH 5, and adsorbent dosage 0.5g in 10 minutes. From this finding, the activated carbon produced from waste tyre can be used for effective and economic removal of chemical plant wastewater containing toxic 2-CP.

Keywords:
Waste tire, AC, adsorption, 2-chlorophenol

1. Introduction

Many phenolic compounds are regulated as priority pollutants for environmental control because of their high toxicity to human beings even at low concentration exposure [1]. Chlorophenols ˚CPs) constitute an important class of aquatic pollutants that are present in aquatic ecosystems. 2-Chlorophenol ˚2-CP), a low chlorine-substituted phenol and the precursor of the higher-substituted CPs, has been introduced into the environment via anthropogenic activities. Chlorophenols have been extensively used in the production of fungicides, herbicides, insecticides, pharmaceuticals, preservatives, glue, paint, fibers, leather, and as intermediates in chemical synthesis [2]. Exposure to 2-CP may cause carcinogenic and teratogenic properties in humans and the environment. Due to their toxicity and adverse effects upon human and biota, the United States Environmental Protection Agency ˚US EPA) has classified them as toxics or hazardous pollutants [3]. High amounts of chlorinated solvents were found to cause dizziness, reduce the ability to concentrate

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and remember, damage the nervous system, and produce an irregular heartbeat. Thus, it is important to eliminate these compounds before discarding the wastewater into the environment.

Techniques engaged for the removal of chlorophenols from waste water include adsorption [4], catalytic wet oxidation [5], biodegradation [6], ozonation and electrochemical degradation [7]. Among them, adsorption technology is widely considered the most applicable technique for the removal of CPs. However, an appropriate cost-effective material for CPs capture is important. The most widely used adsorbent among the various adsorbents for CPs adsorption is activated carbon because of its low cost, high surface area, and high porosity which can help to enrich the organic substrate around the adsorbent [8]. Obtaining AC from the waste tyre is a great importance since it can lower the cost of commercial ACs, eliminate fire hazard and address pollution problems associated with the disposal process of old tires. Producing AC from waste tyre resulted in high amount of carbon and doubly effective solution for the environmental pollution where it reducing waste in a green way [9]. Activated carbon derived from waste tyre shows high adsorption performance.

The aim of the study was to evaluate the performance of activated carbon produced from waste tyre for the removal of chlorine from 2-CP. As the activated carbon was derived from waste rubber tires, the study is considered a doubly effective solution for environmental pollution. It represents sustainable way to dispose the waste tires and an economic source of carbonaceous material.

2. Methodology

2.1 Materials

All chemicals 2-chlorophenol ˚2-CP), hydrogen peroxide ˚H_2O_2), potassium hydroxide ˚KOH) and hydrochloric acid ˚HCl) were used analytically pure and purchased from Sigma-Aldrich. The waster rubber tyre was used as precursor in preparation of AC.

2.2 Preparation of Activated Carbon from Waste Tyre

The waste rubber tyre was cut into small pieces and washed thoroughly with distilled water, then then dried in an oven at 105°C for 2 h. The granule was heated up to 300°C in furnace for 3 h to separate the black tire crude oil, distilled diesel oil and produced oil. Then, the activations of char was take place at 500°C for 5 h in 200 $mlmin^{-1}$ of nitrogen gas. Then, the chars recovered from the pyrolysis reactor was treated with hydrogen peroxide solution. For this purpose, the product treated with H_2O_2 ˚6% concentration) with a ratio of 1 g/20 mL carbon/H_2O_2. The mixture ˚carbon and acid solution) was stirred and heated at 100°C for 24 h in oven. Then, the sample washed thoroughly with deionized water and dried at 110°C for 2h to form activated carbon.

2.3 Characterization of Adsorbent

The characteristics of the synthesized catalysts were investigated using XRD, BET, FESEM and FTIR. The X-ray diffraction ˚XRD) was used to determine the crystalline structure of the AC in the range of $2\theta = 10 – 80^o$ with Cu Kα radiation ˚λ = 1.5405Å). The measurement of BET surface area, pore diameter and pore volume for AC were conducted using AUTOSORB-1 model AS1 MP-LP instrument at 77 K. The surface morphology of the AC was analyzed 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 cm^{-1}.

2.4 Batch Adsorption Procedure

The equilibrium adsorption studied by using batch mode adsorption. A constant mass of adsorbent ˚0.1 g) was contacted with 50 mL of 2-CP solutions of 10mg/L. The bottles were sealed and placed in a shaker until equilibrium was reached. Samples were then withdrawn for every 5 minutes of reaction by syringe, filtered through 0.22m syringe filter, and diluted to the required level for analysis. Similar adsorption procedure was repeated by varying the initial pH of 2-CP solution ˚3, 5, 7, and 10) and adsorbent dosage ˚0.05g, 0.1 g, 0.3g and 0.5g). The percentage removal of CPs ˚R%) calculated.

2.5 Analysis of 2-Chlorophenol

Samples were analysed using a Varian Cary 1E UV/Vis spectrophotometer at their maximum wavelength of 284nm. The equilibrium amount of CPs adsorbed per unit mass of adsorbent, qe (mg/g), at different 2-CP concentrations was identified using the following equation.

$$qe = \frac{(\mathrm{Co} - \mathrm{Ce})\mathrm{V}}{W} \quad (1)$$

where qe (mg/g) is the equilibrium amount of adsorbate (CPs) adsorbed per unit mass of adsorbent (AC) ; V (L) is the volume of the solution and W(g) is the mass of the adsorbent used.

The percentage removals (% R) of the adsorbates (CPs) in solution calculated using the following

$$\mathrm{CPsremoval}\ (\%) = \frac{\mathrm{Co} - \mathrm{Ce}}{\mathrm{Co}} \quad (2)$$

where Co and Ce are the liquid-phase concentrations at initial and equilibrium states (mg/L), respectively.

3. Results and Discussion

3.1 Characterization of AC

Figure 1 shows XRD pattern for the AC adsorbent produced from waste tyre. The result indicates the presence of two peaks at 2ϑ = 25.43 and 43.89. The peaks were appeared in the pattern due to the presence of amorphous carbon that caused by disordered stacked of carbon ring [10].

The isotherms produced by AC showed type IV adsoption characteristics according to IUPAC classification [4]. The hysteresis loop was determined to be type H3 due to the type of capillary condensation taking place in its mesopores. Type IV isotherm is usually attributed to monolayer-multilayer adsorption since it follows a similar part of the corresponding part of a Type II isotherm obtained with the given adsorptive on the similar surface area as the adsorbent in a non-porous form [10]. Table 2 summarizes the BET surface area and pore volume and pore diameter of the researched adsorbent. According to the results, AC produced in the current research possesses high specific surface area (208 m^2/g) and average pore volume (0.5817 cm^3/g) compared the other adsorbents. However, the average pore diameter for the current researched catalyst is the highest. This indicates that the synthesis of AC using waste tyre as precursor can give high surface area which can increase the adsorption capacity.

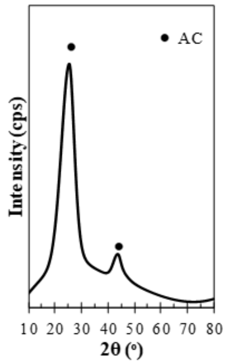

Fig. 1. XRD analysis of AC

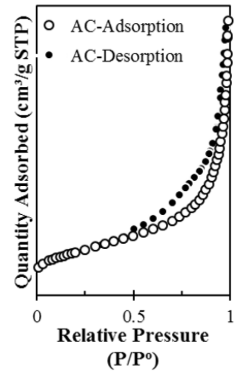

Fig. 2. N_2 adsorption-desorption isotherm for AC

Table 2
Comparison of properties of AC

Adsorbents	BET surface area ˚m^2/g)	Pore volume ˚cm^3/g)	Average pore diameter ˚Å)	Researchers
AC	62	0.9592	615	[11]
ACZnO	15	0.3041	802	[11]
ZrSAC$_4$	115	0.0800	N/A	[12]
AC	208	0.5817	126	Current Research

The morphology of the activated carbon produced from waste rubber tyre was characterized by FESEM, and shows in Figure 3. From the analysis, the morphological region of the AC is granular with particle diameter between 80-100 nm. High resolution of the image of the developed activated carbon indicates that there are different pore structures in the adsorbent. High surface area and pore structure of the AC were effective to be as an adsorbent. When the porosity increases, the surface area also increases [11].

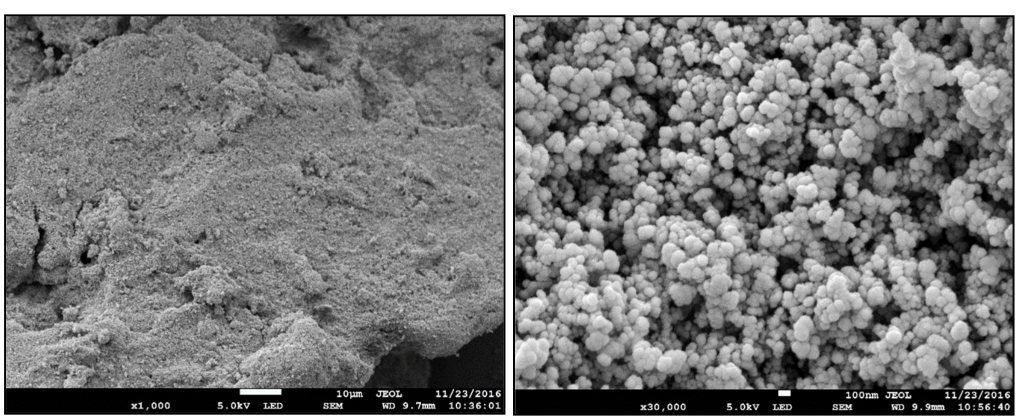

Fig. 3. FESEM images under magnification (a) 1000x and (b) 30000x

Figure 4 shows the FTIR spectrum for AC. The first peak at 2665 cm^{-1} indicates the strong bonded functional group of O-H and C-H stretching absorption. Next, the band centered on 1992 cm^{-1} indicates enhancement in the aromatic C=C groups (carbonization). Then the peak at 997 cm^{-1} represents C-O stretching functional group. 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 [13, 14].

3.2 Adsorption Study on AC
3.2.1 Effect of initial 2-CP concentration

The effect of concentration on the adsorption capacity of chlorinated hydrocarbons by using AC at different concentrations is illustrated in Figure 5. The adsorption of chlorinated hydrocarbons rapidly increased with contact time and then proceeded at a slower rate until the equilibrium was achieved. Fixed amount of adsorbent dosage (0.1g) used in this experiment whereby concentrations of adsorbate were manipulated. The rapid adsorption was achieved at 10 ppm (mg/L). The adsorption process takes place rapidly at the initial step on the external surface of the adsorbent followed by a slower internal diffusion process [15]. The rapid adsorption at the initial step is due to the presence of a large number of vacant active sites observed after a certain time indicated that the uptake of the solute molecules was made difficult due to the repulsive forces between the solute molecules on the surface of the AC as well as in the bulk phases. Longer contact times were required for solutions of higher initial concentrations to reach equilibrium [16].

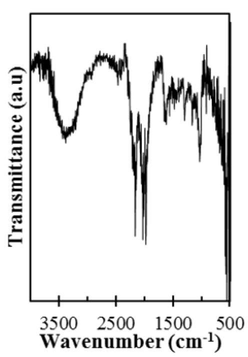

Fig. 4. FTIR spectrum of the AC

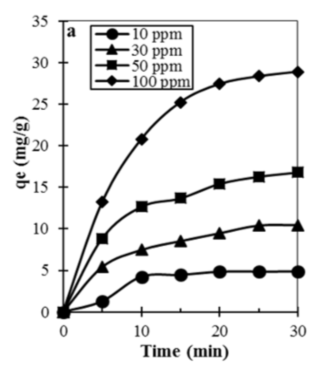

Fig. 5. Effect of contact time on adsorption at different concentrations

3.2.1 Effect of pH

Figure 6 indicates the influences of pH on adsorption of 2-CP. Removal of chlorinated hydrocarbons were examined in pH range between 3 to 10. Adsorption was attributed to the acidic character of the solute molecules. In terms of pH, it signifying that endothermic nature of the process with acidic solution pH being the most favorable for the adsorption where its capacity increase at pH 5 because 2-CP is a weak acid and it associated with the electron withdrawal effect of the chlorine substitution on the aromatic ring thus reducing the overall electron density of the aromatic ring of the adsorbate [17, 18].

3.2.1 Effect of adsorbent dosage

The amount of the adsorbent is considered a significant factor because it can identify the capacity of the adsorption for a given initial concentration of the adsorbate. The effect of AC dosage on the adsorption of chlorinated hydrocarbons illustrated in Figure 7. Various adsorbent dosage utilized for adsorption of 2-CP at initial concentration 10 mg/L, temperature 25 °C and shaking time 30 min. The result shows that as the adsorbent dosage increased, the percent removal of chlorinated hydrocarbons increased from 96.98% to 99.43%. As seen in figure below, increase in adsorption sites for a constant concentration relatively increase the performance on AC on adsorption of 2-CP.

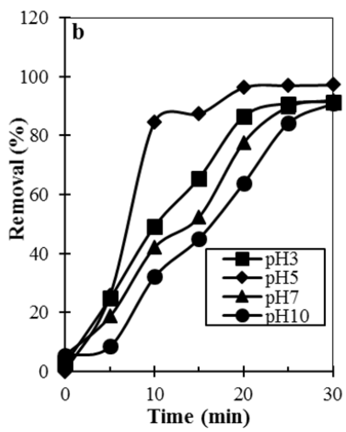

Fig.6. Effect of pH on removal efficiency of 2-CP

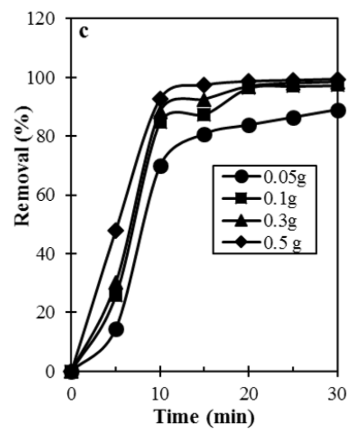

Fig. 7. Effect of adsorbent dosage on removal efficiency of 2-CP

4. Conclusion

This research has notably demonstrated the effective performance of AC derived from waste rubber tyres for the removal of 2-chlorophenol. AC was characterized by the means of XRD, BET, FESEM and FTIR indicated AC have high adsorption capacity. Adsorption studies showed that rapid adsorption of chlorine from 2-CP was achieved with 0.5g of adsorbent dosage at 10 ppm and pH 5. The studies reveal that AC derived from waste rubber tyres possess high adsorption capacity hence it could be employed effectively as low-cost adsorbents for removal of chlorophenols.

Acknowledgments

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