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Activated Carbon Based on *Borassus aethiopum* Shells, Hulls, Kernels and Fruits for Removal of Phenol and 2-Chlorophenol from Water

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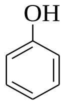
Abstract

This study aimed at developing activated carbons from *Borassus aethiopum* shells (BaS), hulls (BaH), kernels (BaK) and fruits (BaF) for removing phenol (Ph) and 2-chlorophenol (2-CP) from aqueous solution. The preparation of the activated carbons involved carbonization of the starting materials at 500 ºC followed by chemical activation at 600 ºC using 0.5 M H_3PO_4 acid. The prepared activated carbons were found to be mesoporous having pore sizes and surface areas in the range of 3.2 to 3.5 nm and 644 to 740 m^2/g, respectively. Thermogravimetric analysis (TGA) thermograms showed that the prepared activated carbons can be applied in the batch solution with a temperature not greater than 500 ºC as above this temperature, the materials decompose. Adsorption experiments showed that the uptake of 100 mg/L of Ph and 2-CP from water is favourable using an adsorbent dose of 0.5 g and a contact time of 6 hours. On the other hand, the batch solution of pH 8 and 6 favoured the adsorption of Ph and 2-CP, respectively. Moreover, the adsorption of the aforementioned adsorbates strongly depended on their initial concentrations and temperature of the batch solution. Equilibrium adsorption isotherms fitted into both Langmuir and Freundlich isotherms, but the Freundlich adsorption model was found to have the highest regression value, hence the best fit.

Keywords: Adsorption, Activated Carbon, Carbonization, Activation, *Borassus aethiopum*.

Introduction

Phenol is one of the first compounds inscribed into the list of priority pollutants by the US Environmental Protection Agency with concentrations of approximately 0.01 to 2.0 µg/L in natural waters (Michałowicz and Duda 2007). Acute exposure to phenol (**1**) is known to cause gastrointestinal discomfort, skin irritation and headache, while long term exposure to phenol can be toxic to the nervous system, kidney and liver (Pradeep et al. 2015). Phenol may exist as chlorophenols (**2**), nitrophenols (**3**), methyl phenols (**4**), aminophenols (**5**), bisphenols (**6**), catechol (**7**) and chlorocatechols (**8**). Chlorophenols are the most widespread and the largest group of phenols formed in the environment by chlorination of aromatic compounds present in soil and water (Michałowicz and Duda 2007). Chlorophenols make up one of the water-soluble hazardous groups of toxic organic chemicals for living organisms and humans even at low concentrations and are among the priority pollutants of major environmental concern (Fan et al. 2017).



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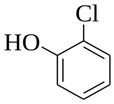

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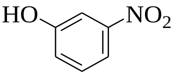

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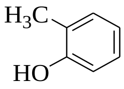

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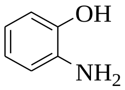

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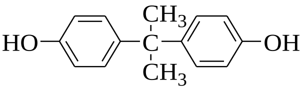

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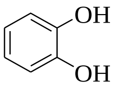

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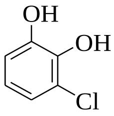

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For a major concern, the removal of phenols from water is inevitable, and various methods classified into advanced and conventional methods have been used to remove phenols from water. Advanced methods are mainly based on the oxidation processes in destroying phenols and they include electrochemical, photochemical, chemical oxidation and membrane separation processes (nanofiltration and reverse osmosis) (Mohammadi et al. 2015). Conventional methods are divided into three main categories: biological, chemical and physical methods. Biological methods involve either the use of microorganisms (yeasts, fungi and bacteria) or enzymes (proteins) in degrading phenols to less toxic end products (Pradeep et al. 2015), while chemical methods involve the use of chemicals in removing phenols from water (Mohammadi et al. 2015). The physical method involving adsorption by the use of activated carbon prepared from locally available materials is considered to be the best, effective, low-cost and most frequently used method for the removal of phenols from water (Dakhil 2013). The adsorptive capacities of the activated carbons prepared from different locally available materials do differ; as a result, a search for suitable materials that may result into activated carbon with high capacity of removing phenols from water is of importance.

Numerous researchers have studied on removal of phenol and chlorophenols from water using activated carbon prepared from locally available materials. Dakhil (2013) investigated the adsorption of phenol present in industrial wastewater on locally available sawdust. The findings reported that the percentage removal of phenol increased with increasing adsorbent dosage until it reached an optimal dose, while the percentage removal of phenol decreased as the initial phenol concentration was raised. The removal of phenol increased slightly with increasing the pH value from 3 to 6, then, fast decreased at pH 7 to 9, and the equilibrium happened at 120 minutes. In addition, Dakhil (2013) reported that the equilibrium data agrees well with both Langmuir and Freundlich models. Fan et al. (2017) studied the adsorption of chlorophenols from aqueous solution onto graphene and reported that the adsorption equilibrium was attained at 20 minutes. The equilibrium data fitted well with the Langmuir adsorption model and thermodynamic parameters demonstrated that the adsorption process was endothermic and spontaneous. Hameed and Rahman (2008) derived activated carbon from biomass (rattan sawdust) for the removal of phenol from aqueous solution. Their results showed that the activated carbon prepared had high adsorption capacity with the best Langmuir isotherm fit. Malakootian et al. (2015) evaluated the removal efficiency of 2-chlorophenol in aquatic environment by modified fly ash. In their study they found that the adsorbent prepared was able to remove 96.2 and 82.2% of 2-chlorophenol from synthetic and real wastewater, respectively, under optimized conditions of 0.8 g adsorbent dose, pH of 3, 2 hours contact time at room temperature. Jung et al. (2001) studied the adsorption of phenol and chlorophenols on four commercial granular activated carbons. Characterization of the carbons by several techniques appeared to have the disordered graphitic structure composed of the functional groups such as carbonyl, carboxyl, alcoholic and ether groups. They also estimated that the olefinic double bonds in the carbon skeleton were conjugated with the functional groups on the surface of the activated carbons. In their adsorption study, they realized that the dispersion force between the π-electron of the double bond in activated carbons and the π-electron in phenol and chlorophenols were the main adsorption mechanism. The adsorption isotherm data obtained from their study complied well with Freundlich adsorption isotherm.

Investigations on adsorption of phenols made by various researchers show that activated carbon from various starting materials have different adsorption capacity. Therefore, this study aimed at investigating the feasibility of activated carbons prepared from *B. aethiopum* shells (BaS-AC), *B. aethiopum* hulls (BaH-AC), *B. aethiopum* kernels (BaK-AC) and *B. aethiopum* fruits (BaF-AC) in removing phenolic pollutants from water using phenol and 2-chlorophenol as model components.

Materials and Methods

Sample collection

Borassus aethiopum fruits were collected from Ifakara in Morogoro Municipality and were transported to the laboratories of Chemistry Department, University of Dar es Salaam for further processing to obtain BaS, BaH, BaK and BaF.

Chemicals

Phosphoric acid (85%), phenol (90%), 2-chlorophenol (99.5%), hydrochloric acid (37%) and sodium hydroxide (99%) were bought from reputable suppliers (Sigma Aldrich, UK) and used without further purification. Distilled water was obtained from Chemistry Department, University of Dar es Salaam.

Methods

Preparation of the activated carbons by chemical activation

Preparation of BaS-AC, BaH-AC, BaK-AC and BaF-AC involved washing of BaS, BaH, BaK and BaF with warm water, rinsing with distilled water, drying at 105 °C for 3 h in an oven and cooling prior to the carbonization. Thereafter, separate samples of the dried and weighed BaS, BaH, BaK and BaF were carbonized in a muffle furnace at a temperature of 500 °C for 3 h and the charred products were weighed after being allowed to cool. Then, the mass of 50 g of carbonized BaS, BaH, BaK and BaF were impregnated with 150 mL of 0.5 M H_3PO_4 for 3 hrs. The resulting moist paste upon mixing the char with phosphoric acid was charged into the muffle furnace and heated to activation temperature of 600 °C. After the chemical activation, BaS-AC, BaH-AC, BaK-AC and BaF-AC were rinsed thoroughly with distilled water to remove the remaining phosphoric acid and ash. BaS-AC, BaH-AC, BaK-AC and BaF-AC were then dried in an oven at a temperature of 110 °C for 3 hours. The prepared BaS-AC, BaH-AC, BaK-AC and BaF-AC were crushed into powder and sieved using 250 µm sieves.

Adsorption experiments

The effect of varying adsorbent dose, initial adsorbate concentration, contact time, pH and temperature were investigated. The adsorption capacity (q_e) and removal efficiency (%*R*) at the equilibrium of the prepared adsorbents were calculated using Equations 1 and 2, respectively (Okuofu and Osakwe 2012). For the effect of pH, the solution was adjusted using 0.2 M NaOH and 0.1 M HCl.

$$q_e = \left(\frac{C_o - C_e}{m}\right) \times V \qquad (1)$$

$$\%R = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad (2)$$

where, C_o and C_e are initial and equilibrium concentrations (mg/L) of Ph and 2-CP, *V* is the volume (L) of Ph and 2-CP solutions and *m* is the mass (mg) of BaS-AC, BaH-AC, BaK-AC and BaF-AC.

The effect of the adsorbent dose was studied by adding varying masses of 100, 200, 300, 400, 500 and 600 mg of the adsorbents to 6 conical flasks containing 50 mL of 100 mg/L Ph and 2-CP solutions at room temperature. The effect of initial concentration of Ph and 2-CP was studied using 500 mg of each adsorbent with 50 mL of each 100 mg/L, 130 mg/L, 160 mg/L, 190 mg/L and 220 mg/L of Ph and 2-CP solutions. The effect of contact time was studied by contacting 500 mg of each adsorbent with 50 mL of the 100 mg/L Ph and 2-CP solutions at room temperature at different time intervals of 60, 120, 180, 240, 300 and 360 minutes. The effect of adsorbate pH was studied at pH of 3, 5, 7, 8 10 and 11 at room temperature. The effect of solution temperature was studied at the temperatures of 28, 40, 50, 60, and 70 ºC for 6 hrs contact time. For each test, the contents of the flasks were filtered and analyzed for equilibrium concentration using UV-Vis spectrophotometer.

Results and Discussion

Characterization of the prepared activated carbons

ATR–FTIR analysis

The FT-IR spectral results for CBaS and BaS-AC in Figure 1 show the effect of acid treatment on CBaS as well as the composition of various functional groups of the BaS-AC, which could be responsible for the binding of Ph and 2-CP. The remarkable peak at 1737–1545 cm^{-1} was observed, a characteristic for a carbonyl functionality (C=O) stretching, a peak at 3019 cm^{-1} a characteristic for $-$OH stretching vibration, a peak at 1366 cm^{-1} a characteristic for C$-$C stretching and a peak at 1206 cm^{-1} a characteristic for C=C stretching (Foya et al. 2014). When CBaS was activated at 600 °C, there was a slight variation in the peak pattern but a peak at 3019 cm^{-1} disappeared as a result of acid dehydration. In addition, the new band shifts upon activation were observed at a peak of 1133 cm^{-1} and 1038 cm^{-1} which may be assigned as P=O or P$-$O$-$P stretching vibration, which may be introduced by the activating agent (H_3PO_4) (Yakout and El-Deen 2016).

FT-IR spectral results (Figure 2) showed a band shift which implies that there was a structural modification of the CBaH upon acid activation. It also showed the functional groups present on BaH-AC surface. A peak at 1559 cm^{-1} was observed, a characteristic for C=O stretching, a peak at 1375 cm^{-1} a characteristic for a lignin (Prasad et al. 2011) and a peak at 1080 cm^{-1} a characteristic for C$-$O stretching (Nabais et al. 2011). After treating CBaH with phosphoric acid a peak at 1375 cm^{-1} disappeared.

FT-IR spectral results of CBaK and BaK-AC showed a peak at 1548 cm^{-1}, a characteristic for C=O stretching, a peak at 1252 cm^{-1} which can be assigned to C$-$O$-$C stretching and a peak at 1114 cm^{-1} was also observed, a characteristic for C$-$O or O$-$H stretching (Przepiórski et al. 2004) (Figure 3). Likewise, FT-IR spectral results for CBaF and BaF-AC showed a peak at 1560 cm^{-1} ascribed to C=N stretching and a peak at 1099 cm^{-1} attributed to C=O stretching (Przepiórski et al. 2004) (Figure 4). Furthermore, the bands in the range 900–700 cm^{-1} observed in all prepared activated carbons can be attributed to C–H deformation due to out-of-plane vibrations (Nabais et al. 2011).

Porosity analysis

Porosity analysis involved the determination of the surface area, pore diameter, pore volume, type of adsorption isotherm and pore size distribution of the prepared activated carbons. The surface areas of the BaS-AC, BaH-AC, BaK-AC and BaF-AC investigated by nitrogen adsorption-desorption technique at 77 K using the BET method at a relative pressure (P/P_o) range of 0.05 to 0.15 were found to range from 644.59–737.88 m^2/g (Table 1). These results are in good agreement with the surface areas reported by Garba and co-workers (2014). Pore diameter and pore volumes obtained using Barrett, Joyner and Halenda (BJH) method were found to be in the range of 3.21–3.49 nm and 0.56–0.64 cm^3/g, respectively.

The prepared activated carbons are mesoporous as they have the pore diameter in the range of 3.21–3.49 nm (Garba et al. 2014). The activated carbons prepared have different BET surface area, pore volume and pore diameter because they have been prepared from different parts of *B. aethiopum* fruits which may have different carbon content and volatile matter compositions.

Table 1: Summary of porosity results

Material	SA_{BET} (m²/g)	BJH pore volume (cm^3/g)	BJH pore diameter (nm)
BaS-AC	644.593	0.644	3.486
BaH-AC	737.883	0.563	3.209
BaK-AC	665.674	0.617	3.493
BaF-AC	712.636	0.573	3.214

Thermogravimetric analysis

The TGA curves (Figures 5 and 6) showed the increase in thermal stability for all carbonized materials upon acid activation. The thermal stability for all activated carbons (BaS-AC, BaH-AC, BaK-AC and BaF-AC) increased to 500 °C from about 300, 380, 400 and 400 °C of CBaH, CBaF, CBaS and CBaK, respectively. All adsorbents showed a small change in mass from room temperature to about 130 °C, which may be attributed to the loss of moisture contents of the materials. Moreover, the change in mass was observed from 300 °C (CBaH), 380 °C (CBaF), 400 °C (CBaK), 400 °C (CBaS), 500 °C (BaS-AC), 500 °C (BaH-AC), 500 °C (BaK-AC) and 500 °C (BaF-AC) to about 500, 570, 580, 600, 660, 600, 640 and 650 °C of acid activated materials, respectively. This may be attributed to the loss of organics and functional groups of the activated carbons. No more change in mass was observed above 500 °C (CBaH), 580 °C (CBaS, CBaK and CBaF) and 630 °C (BaS-AC, BaH-AC, BaK-AC and BaF-AC), implying that all the carbon had burnt off leaving the inorganic compounds in the form of ash. From the TGA data, it was confirmed that the activated carbons prepared can be used in a batch solution temperature not greater than 500 °C, because beyond this temperature they start to decompose, leading to the loss of some important functional groups responsible for adsorption process.

Adsorption studies

Effect of adsorbent dose

The adsorbent doses were varied from 100, 200, 300, 400, 500 and 600 mg in 50 mL of 100 mg/L aqueous solution of Ph and 2-CP to determine a suitable dose for maximum adsorption of Ph and 2-CP. In each case, the increase in adsorbent dose resulted in an increase in percentage removal and adsorption capacity of Ph and 2-CP (Figures 7 and 8, respectively). However, for the adsorption of Ph, it was observed that above 400 mg adsorbent dose, the removal efficiency, as well as adsorption capacity, did not increase significantly; an indication that no Ph molecules are left to be adsorbed with the excess adsorbent dose. The maximum percentage removal and adsorption capacity of Ph were found to be 71.41% and 7.14 mg/g using BaS-AC at the optimal dose of 400 mg, 91.91% and 9.19 mg/g using BaH-AC at the optimal dose of 300 mg, 68.69% and 6.87 mg/g using BaK-AC at the optimal dose of 400 mg and 88.42% and 8.84 mg/g using BaF-AC at the optimal dose of 400 mg, respectively.

For the removal of 2-CP the maximum percentage removal and adsorption capacity were found to be 73.93% and 7.39 mg/g for BaS-AC at the optimal adsorbent dose of 400 mg, 94.58% and 9.46 mg/g for BaH-AC at the optimal adsorbent dose of 300 mg, 65.64% and 6.56 mg/g for BaK-AC at the optimal adsorbent dose of 500 mg and 89.24% and 8.92 mg/g for BaF-AC at the optimal adsorbent dose of 400 mg, respectively. It was observed that for both Ph and 2-CP adsorption, BaH-AC had the higher percentage of removal and adsorption capacity. This may be attributed to its high BET surface area as shown in Table 1. Furthermore, it was found that for all adsorbents (BaS-AC, BaH-AC, BaK-AC and BaF-AC) the removal of the Ph and 2-CP was achieved with an adsorbent dosage of between 100 mg and 500 mg. Beyond 500 mg, the increase in percentage removal and adsorption capacity of Ph and 2-CP for all adsorbents were found to be relatively insignificant, hence the optimum dose for all adsorbents was fixed at 500 mg. The variations in percentage removal and adsorption capacity between BaS-AC, BaH-AC, BaK-AC and BaF-AC could be related to the type of functional groups and porosity of the adsorbents (Okuofu and Osakwe 2012). The phenomenon of increase in percentage removal and adsorption capacity of Ph and 2-CP with an increase in adsorbent dosage may be explained by the increase in the number of active sites that are available for adsorption (De Gisi et al. 2016).

Effect of initial adsorbate concentration

Figure 9 shows that with an increase in Ph and 2-CP concentrations from 100 mg/L to 220 mg/L, there was a decrease in the percentage removal of Ph and 2-CP for all adsorbents. The percentage removal of Ph decreased from 78.82 to 60.62% for BaS-AC, from 93.75 to 84.42% for BaH-AC, from 76.29 to 54.45% for BaK-AC and from 87.75 to 74.22% for BaF-AC. The percentage removal of 2-CP decreased from 78.85 to 59.03% for BaS-AC, from 88.93 to 75.64% for BaH-AC, from 73.01 to 56.12% for BaK-AC and from 87.43 to 63.54% for BaF-AC.

It is worth to note that adsorption capacity increased with an increase in the initial concentration of Ph and 2-CP (Figure 10). The adsorption capacity of Ph increased from 7.88 to 13.34 mg/g for BaS-AC, from 9.37 to 18.57 mg/g for BaH-AC, from 7.63 to 11.98 mg/g for BaK-AC and from 8.77 to 16.33 mg/g for BaF-AC. The adsorption capacity of 2-CP increased from 7.89 to 12.99 mg/g for BaS-AC, from 8.89 to 16.64 mg/g for BaH-AC, from 7.30 to 12.35 mg/g for BaK-AC and from 8.74 to 15.86 mg/g for BaF-AC. This phenomenon can be explained by the fact that increasing initial Ph and 2-CP concentrations result into an increase of the driving force of the concentration gradient which causes easy passage of Ph and 2-CP molecules from the bulk solution to the particle surface. This leads to higher adsorption capacity since more adsorbate molecules reach the adsorption active sites of the adsorbents and get adsorbed. Decreasing in percentage removal of Ph and 2-CP as its initial concentration was increased is accounted by the saturation of adsorbents active sites as the number of active sites of the adsorbent responsible for adsorption was fixed by keeping constant the adsorbent dose. A similar observation was reported by Banat et al. (2000) when investigating the adsorption of phenol by bentonite, and Malakootian et al. (2015) when evaluating the removal efficiency of 2-chlorophenol in aquatic environments by modified fly ash.

Effect of contact time

The determination of the influence of contact time on the adsorption process is essential in order to ascertain the optimum time required to attain adsorption equilibrium. The effect of contact time was studied by contacting 50 mL of 100 mg/L Ph and 2-CP with 0.5 g of the adsorbents at time intervals of 60–360 minutes. The raw data obtained in the batch adsorption study were used to calculate the adsorption capacity and percentage removal using Equations 1 and 2, respectively. The results obtained were used to plot percentage removal and adsorption capacity as a function of initial adsorbate concentration (Figures 11 and 12,) respectively. It was observed that, increase in contact time from 60 to 240 minutes significantly enhanced the percentage removal and adsorption capacity of Ph and 2-CP using BaS-AC, BaH-AC, BaK-AC and BaF-AC adsorbents. After 240 minutes adsorption rate became slow, indicating that the process approaches the equilibrium state. Therefore, the contact time during adsorption was set to be greater than 240 minutes (360 minutes) to ensure equilibrium is reached. The percentage removal of Ph as adsorption approaches equilibrium was found to be 76.43, 93.56, 71.61 and 89.76% for activated carbon from BaS, BaH, BaK and BaF, respectively; whereas the percentage removal of 2-CP was found to be 87.20, 97.09, 85.63 and 94.93% for activated carbon from BaS, BaH, BaK and BaF, respectively.

On the other hand, as adsorption approaches equilibrium adsorption capacity of Ph was found to be 7.64, 9.36, 7.16 and 8.98 mg/g for activated carbon from BaS, BaH, BaK and BaF, respectively; whereas the adsorption capacity of 2-CP was found to be 8.72, 9.71, 8.56 and 9.49 mg/g for activated carbon from BaS, BaH, BaK and BaF, respectively. For both Ph and 2-CP adsorption, BaH-AC was found to have a higher percent removal and adsorption capacity as adsorption approaches equilibrium state which may be due to its high surface area, indicating that the surface texture and chemistry offers favourable conditions for adsorption.

From the study, it was also observed that the removal of Ph and 2-CP by adsorption onto BaS-AC, BaH-AC, BaK-AC and BaF-AC increased rapidly in the beginning and then slowly until equilibrium. This is in agreement with the findings of Afsharnia et al. (2016). In practice, the adsorption is fast at the first stages of the adsorption process, but slows as the equilibrium state is approached. This phenomenon may be interpreted as; at the first stages of the adsorption process more adsorbent's active sites are available for adsorption, which get saturated as adsorption proceeds (Afsharnia et al. 2016).

Effect of the batch solution pH

Determination of the effect of the pH of a batch solution is important for adsorptive removal of Ph and 2-CP; since it has direct impact on the degree of ionization of the adsorbates and surface charge of the adsorbents. As inferred from Figures 13 and 14, increasing the adsorbate pH from 4 to 8, the percentage removal and adsorption capacity of Ph also increased. Above pH of 8 for BaS-AC, BaH-AC, BaF-AC and BaK-AC, the percentage removal and adsorption capacity of Ph decreased. On the other hand, the percentage removal and adsorption capacity of 2-CP for all adsorbents decreased at the adsorbate pH greater than 6. These results are in agreement with the findings of Moreno-Castilla et al. (1995). The trend on the effect of pH can be explained by the changes on the surface charge of the activated carbons resulting from the increase in the pH of the solution.

At low pH, activated carbons used progressively acquire negative charge on their surfaces. This variation in the surface charge density affects their adsorption capacity because when the adsorbates are dissociated get repelled by the negative charge on the surface of the activated carbons. The adsorbates (Ph and 2-CP) start to dissociate at a pH close to their pKa of 9.96 and 8.8, respectively (Moreno-Castilla et al. 1995). This is a consequence of the fact that the above-mentioned negative charge gradient sets in at approximately two pH units lower (Moreno-Castilla et al. 1995). At pH values greater than 10 activated carbon surfaces are negatively charged and the adsorbates get more dissociated hence, creating much repulsion between the adsorbents and adsorbates. Therefore, the amount adsorbed above the pH of 10 is very low in all cases. This agrees with the findings of Dakhil (2013).

The maximum percentage removal for the removal of Ph was found to be 83.55, 91.96, 78.40 and 90.01% for activated carbon from BaS, BaH, BaK and BaF, respectively at the pH of 8; whereas the maximum percentage removal of 2-CP was found to be 75.85, 91.31, 70.37 and 83.38% for activated carbon from BaS, BaH, BaK and BaF, respectively at the pH of 6. On the other hand, the adsorption capacity of Ph was found to be 8.36, 9.20, 7.84 and 9.00 mg/g for activated carbon from BaS, BaH, BaK and BaF, respectively at the pH of 8; whereas the adsorption capacity of 2-CP was found to be 7.59, 9.13, 7.04 and 8.34 mg/g for activated carbon from BaS, BaH, BaK and BaF, respectively at the pH of 6.

Effect of the batch solution temperature

The change in batch solution temperature can either enhance or reduce the adsorptive uptake of the adsorbate depending on the kind of adsorption process; whether it is endothermic or exothermic. The adsorptive uptake of Ph and 2-CP was found to increase with increasing batch solution temperature from 40 to 70 °C, indicating the endothermic nature of the adsorption process (Figures 15 and 16). This observation may be attributed to the increase in the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle as solution temperature increases (Tan et al. 2009). The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of adsorbate molecules into the pores of the activated carbons at higher temperatures. Senthilkumaar et al. (2006) and Tan et al. (2009) also noted similar observations and they suggested that the increase in adsorption capacity with increase in temperature might be due to the possibility of an increase in the porosity, total pore volume and number of active sites of the adsorbent as well as an increase in the mobility of the adsorbate molecules.

Equilibrium adsorption isotherm

Langmuir and Freundlich adsorption isotherms are widely used in explaining the adsorption process in solid/liquid systems (Afsharnia et al. 2016). The equilibrium adsorption mechanistic behaviour for Ph and 2-CP onto BaS-AC, BaH-AC, BaK-AC and BaF-AC was studied by fitting experimental data of equilibrium concentration (C_e) and adsorption capacity (q_e) to Langmuir and Freundlich adsorption equations (Equations 3 and 4, respectively). In determining the isotherm that fits well to the adsorption process, the isotherms were compared based on their values of correlation coefficient (R).

$$\frac{1}{q_\mathrm{e}} = \frac{1}{q_\mathrm{m} K_\mathrm{L} C_e} + \frac{1}{q_\mathrm{m}} \qquad (3)$$

$$\ln q_\mathrm{e} = \frac{1}{n} \ln C_\mathrm{e} + \ln K_\mathrm{F} \qquad (4)$$

Langmuir adsorption isotherm

In establishing if the adsorption process follows the Langmuir adsorption model, the slopes, y-intercepts and coefficient of determination (R^2) of the linear plots of $1/q_e$ against $1/C_e$ of the adsorbents (Figures 17 and 18) were used to determine the Langmuir parameters presented in Table 2. The Langmuir correlation coefficient (R) was found to be 0.9768, 0.9963, 0.9287 and 0.9797 for the adsorption of Ph; 0.9690, 0.9992, 0.9822 and 0.9850 for the adsorption of 2-CP on BaS-AC, BaH-AC, BaK-AC and BaF-AC, respectively. The maximum adsorption capacity, q_m was 15.97, 22.62, 13.00 and 19.65 mg/g for the adsorption of Ph; 15.17, 21.98, 15.50 and 18.55 mg/g for the adsorption of 2-CP on BaS-AC, BaH-AC, BaK-AC and BaF-AC, respectively. Langmuir constants, K_L for BaS-AC, BaH-AC, BaK-AC and BaF-AC were found to be 0.044, 0.111, 0.055 and 0.063 L/mg for the adsorption of Ph; 0.048, 0.062, 0.032 and 0.068 L/mg for the adsorption of 2-CP, respectively. In addition, the Langmuir separation factor, R_L for initial Ph and 2-CP concentration at a range of 100 to 220 mg/L was found to range from 0.038 to 0.157 and 0.059 to 0.194, respectively. The high value of R indicated that the uptake of Ph and 2-CP occurred on the homogenous adsorption sites of BaS-AC, BaH-AC, BaK-AC and BaF-AC by monolayer adsorption (Dada et al. 2012). The values of R_L for the initial Ph and 2-CP concentration in the range of 100–220 mg/L indicate favorable sorption of Ph and 2-CP onto the BaS-AC, BaH-AC, BaK-AC and BaF-AC because the values are in the favourable range of $0 < R_L < 1$ (Olambo et al. 2016).

Freundlich adsorption isotherm

In testing whether the adsorption process obeys Freundlich adsorption model, the slopes, y-intercepts and coefficient of determination (R^2) of the linear plot of $\ln q_e$ against $\ln C_e$ (Figures 19 and 20) were used to determine the Freundlich parameters in Table 3. The Freundlich correlation coefficient (R) was found to be 0.9954, 0.9974, 0.9718 and 0.9967 for the adsorption of Ph; 0.9917, 0.9853, 0.9956 and 0.9993 for the adsorption of 2-CP on BaS-AC, BaH-AC, BaK-AC and BaF-AC, respectively. The Freundlich constants related to adsorption capacity, K_F were found to be 2.42, 4.59, 2.69 and 3.05 mg/g for the adsorption of Ph; 2.59, 3.58, 1.86 and 3.32 mg/g for the adsorption of 2-CP on BaS-AC, BaH-AC, BaK-AC and BaF-

AC, respectively. The Freundlich constant, which describes the adsorption intensity was found to be 2.63, 2.50, 3.16 and 2.42 for the adsorption of Ph; 2.79, 2.52, 2.44 and 2.64 for the adsorption of 2-CP on BaS-AC, BaH-AC, BaK-AC and BaF-AC, respectively. The value of *n* > 1 reflects a high affinity between adsorbate and adsorbent (Thambavani and Kavitha 2014). The high value of *R* indicates Freundlich isotherm adherence (Dada et al. 2012).

Table 2: Langmuir parameters for the adsorption of Ph and 2-CP on BaS-AC, BaH-AC, BaK-AC and BaF-AC

Adsorbate	Adsorbent	Langmuir parameters			
		q_m (mg/g)	K_L (L/mg)	R_L	***R***
Ph	BaS-AC	15.97	0.044	0.157 to 0.086	0.9768
	BaH-AC	22.62	0.111	0.076 to 0.038	0.9963
	BaK-AC	13.00	0.055	0.133 to 0.071	0.9287
	BaF-AC	19.65	0.063	0.121 to 0.063	0.9797
2-CP	BaS-AC	15.17	0.048	0.146 to 0.079	0.9690
	BaH-AC	21.98	0.062	0.122 to 0.064	0.9992
	BaK-AC	15.50	0.032	0.194 to 0.112	0.9822
	BaF-AC	18.55	0.068	0.114 to 0.059	0.9850

Table 3: Freundlich parameters for the adsorption of Ph and 2-CP onto BaS-AC, BaH-AC, BaK-AC and BaF-AC

Adsorbate	Adsorbent	Freundlich parameters		
		K_F (mg/g)	*n*	*R*
Ph	BaS-AC	2.42	2.63	0.9954
	BaH-AC	4.59	2.50	0.9974
	BaK-AC	2.69	3.16	0.9718
	BaF-AC	3.05	2.42	0.9967
2-CP	BaS-AC	2.59	2.79	0.9917
	BaH-AC	3.58	2.52	0.9853
	BaK-AC	1.86	2.44	0.9956
	BaF-AC	3.32	2.64	0.9993

In a comparison of the two adsorption isotherms, the correlation coefficients of the Langmuir model (Table 2) are lower than that of the Freundlich model (Table 3) which indicates that the Freundlich model is more suitable for interpretation of equilibrium adsorption of Ph and 2-CP on BaS-AC, BaH-AC, BaK-AC and BaF-AC. On the other hand, the parameter 1/*n* is in between 0.1 and 1, showing appropriate adherence to the Freundlich isotherm (Afsharnia et al. 2016). Therefore, the adsorption of Ph and 2-CP on BaS-AC, BaH-AC, BaK-AC and BaF-AC fitted into both Langmuir and Freundlich isotherms, but Freundlich adsorption model was found to have highest regression value, hence the best fits. Similar results were obtained by Dakhil (2013) when investigating the removal of phenol from industrial wastewater using sawdust.

Conclusion

The study aimed at developing activated carbon from *Borassus aethiopum* shells (BaS-AC), hulls (BaH-AC), kernels (BaK-AC) and fruits (BaF-AC) for removing phenol and 2-chlorophenol from water. The activated carbons were prepared by carbonizing the starting materials at 500 °C followed by chemical activation using 0.5 M H_3PO_4 acid at 600 °C activating temperature. The prepared activated carbons were characterised by TGA, FT-IR and N_2 physisorption techniques. TGA analysis showed that the prepared activated carbons can be applied in the batch solution with a temperature not greater than 500 °C. On the other hand, FTIR analysis showed various functional groups present on activated carbon surfaces such as C=O, C-O, C-C, C-H, C=N, P=O, and P-O-P, while N_2 physisorption studies showed that the activated carbons prepared were mesoporous having pore size and surface area in the range of 3.2 to 3.5 nm and 644 to 740 m^2/g, respectively.

Adsorption results indicate that contact time for the adsorption of 100 mg/L phenol and 2-chlorophenol should be not less than 4 hrs for the adsorption equilibrium state to be attained, therefore 6 hrs contact time was used. The adsorption results also indicated that for removing 100 mg/L phenol and 2-chlorophenol, the adsorbent dose of 500 mg is suitable. Moreover, the adsorption of phenol and 2-chlorophenol was maximum at the pH of 8 and 6, respectively. Furthermore, the adsorption was found to increase as the solution temperature increases, indicating endothermic kind of adsorption. The adsorption isotherms showed that the adsorption of phenol and 2-chlorophenol fits to both Langmuir and Freundlich adsorption isotherm. However, there was a strong tendency to obey Freundlich adsorption isotherm, suggesting that the activated carbon surface is heterogeneous.

It can be concluded that BaS, BaH, BaK and BaF precursors are cost effective and active adsorbents for the removal of phenol and 2-chlorophenol from water, BaH being the best over others.

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Appendices

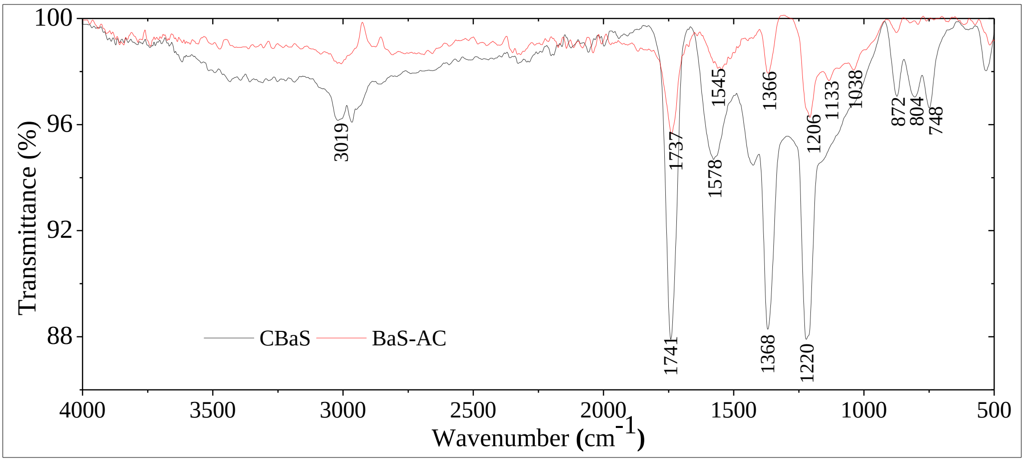

Figure 1: ATR-FTIR spectrum for CBaS and BaS-AC.

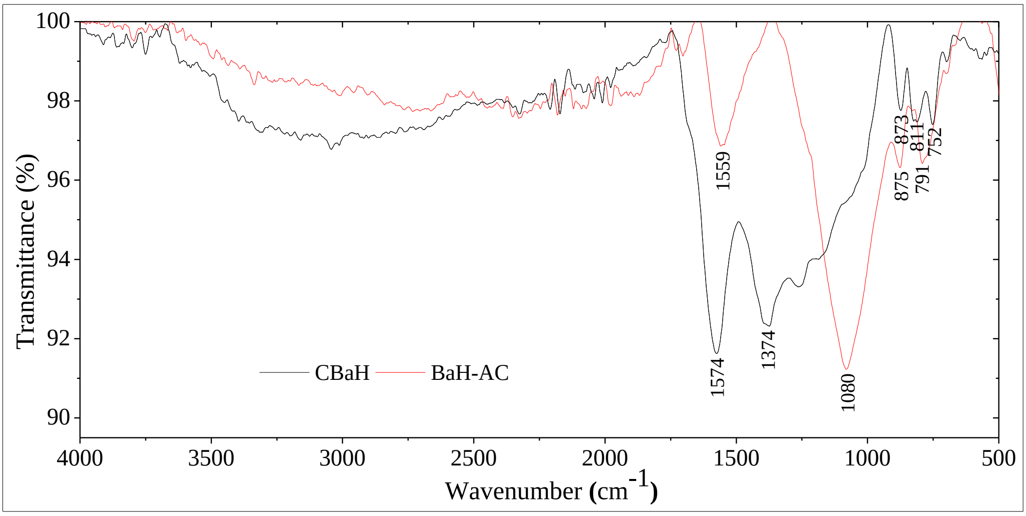

Figure 2: ATR-FTIR spectrum for CBaH and BaH-AC.

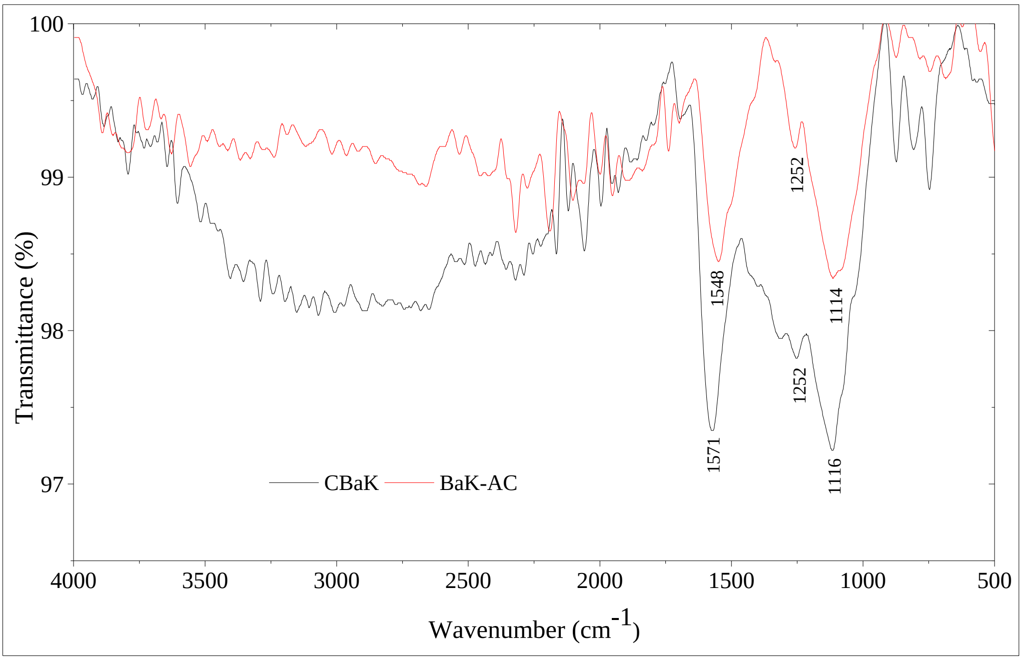

Figure 3: ATR-FTIR spectrum for CBaK and BaK-AC.

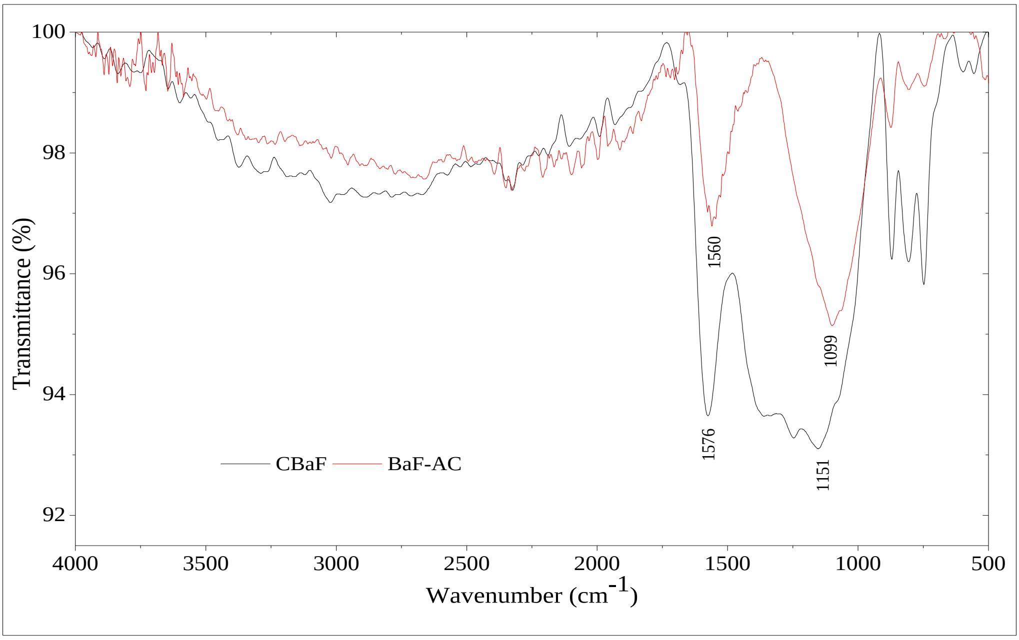

Figure 4: ATR-FTIR spectrum for CBaF and BaF-AC.

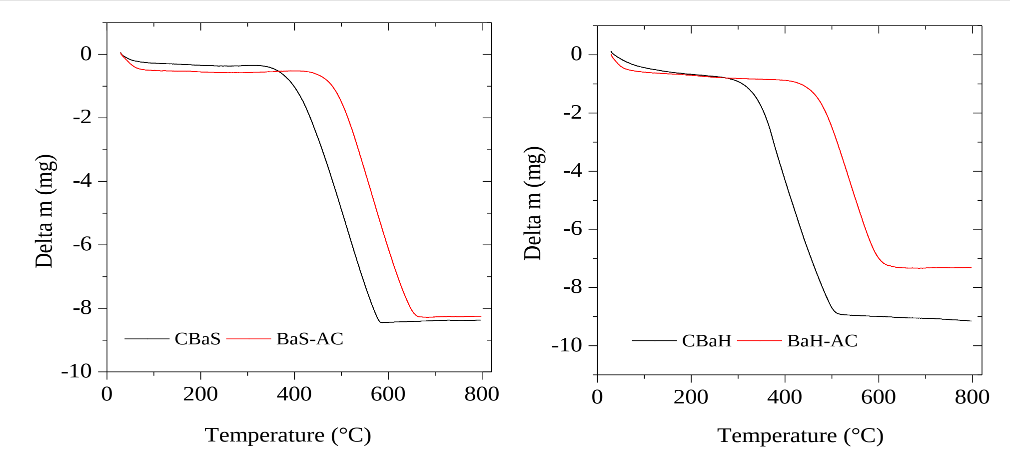

Figure 5: Combined TGA curves for CBaS, CBaH, BaS-AC and BaH-AC.

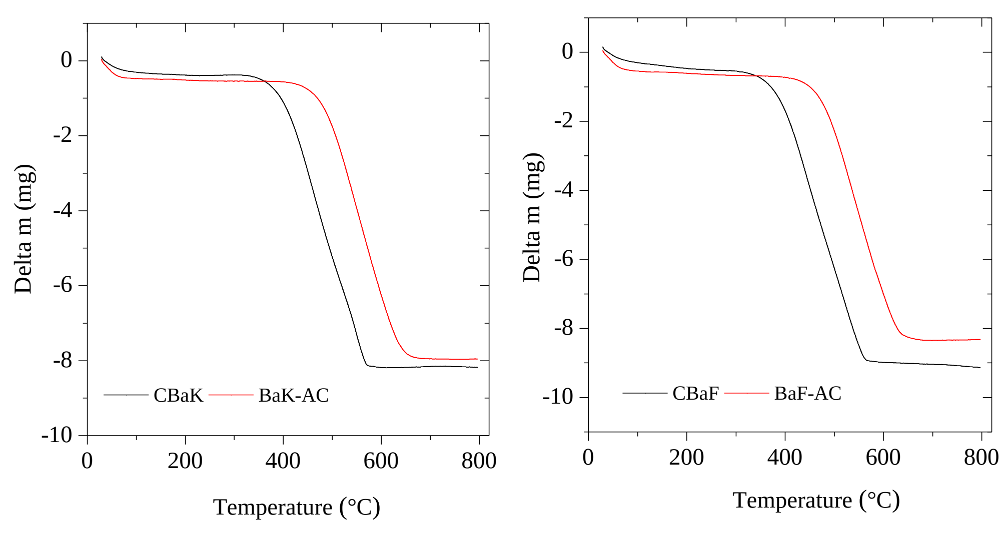

Figure 6: Combined TGA curves for CBaK, CBaF, BaK-AC and BaF-AC.

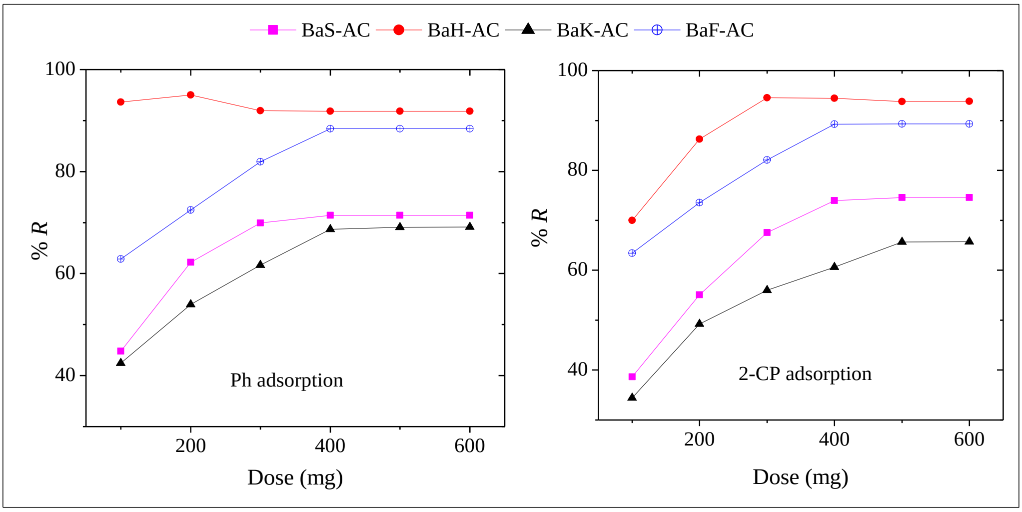

Figure 7: The plot of the effect of adsorbent dose on the percentage removal of Ph and 2-CP (Conditions: 28 °C, 50 mL of 100 mg/L Ph and 2-CP and 6 hrs contact time).

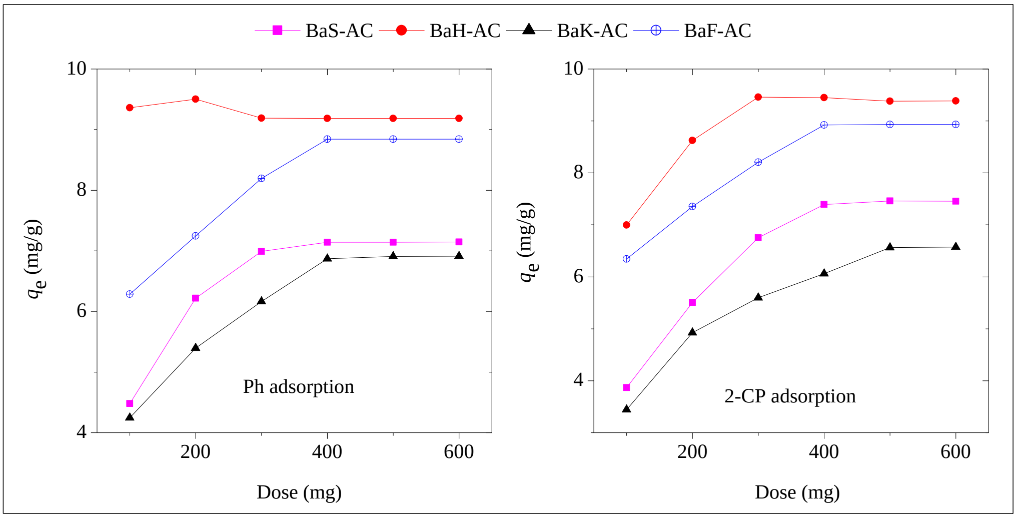

Figure 8: The plot of the effect of adsorbent dose on the adsorption capacity of Ph and 2-CP (Conditions: 28 °C, 50 mL of 100 mg/L Ph and 2-CP and 6 hrs contact time).

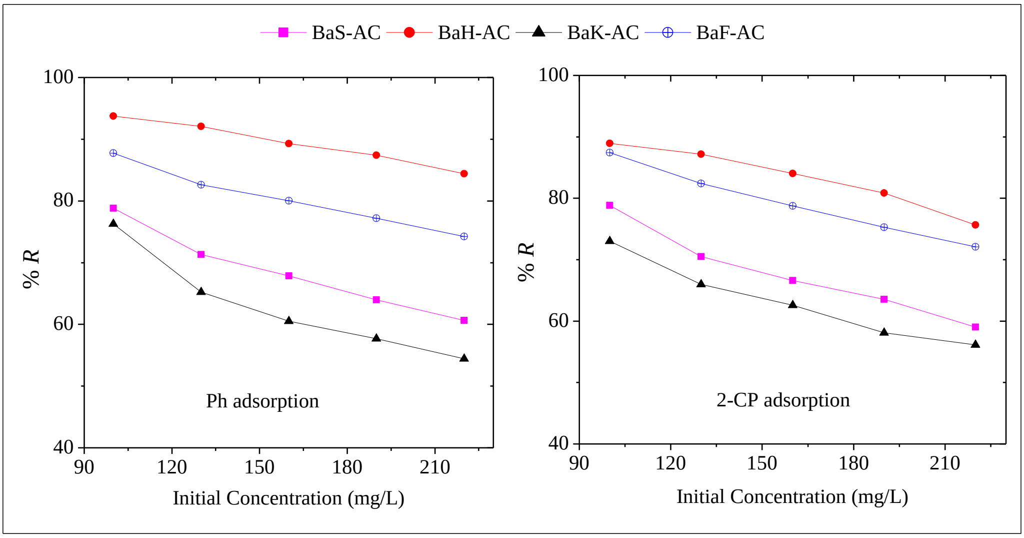

Figure 9: The plot of the effect of initial adsorbate concentration on the percentage removal of Ph and 2-CP (Conditions: 28 °C, 500 mg dose, 50 mL batch volume and 6 hrs contact time).

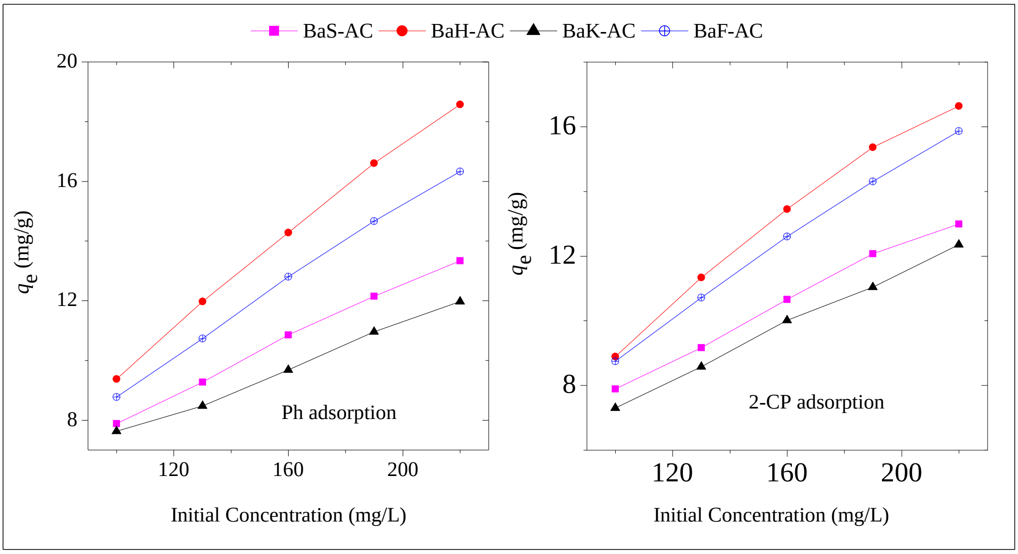

Figure 10: The plot of the effect of initial adsorbate concentration on the adsorption capacity of Ph and 2-CP (Conditions: 28 °C, 500 mg dose, 50 mL batch volume and 6 hrs contact time).

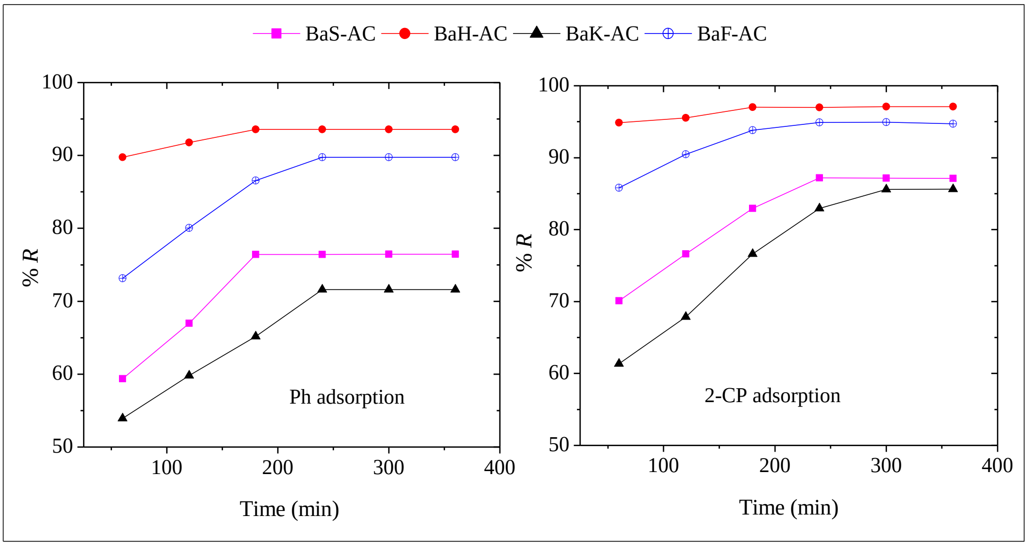

Figure 11: The plot of effect contact time on the percentage removal of Ph and 2-CP (Conditions: 28 °C, 50 mL of 100 mg/L Ph and 2-CP and 500 mg dose).

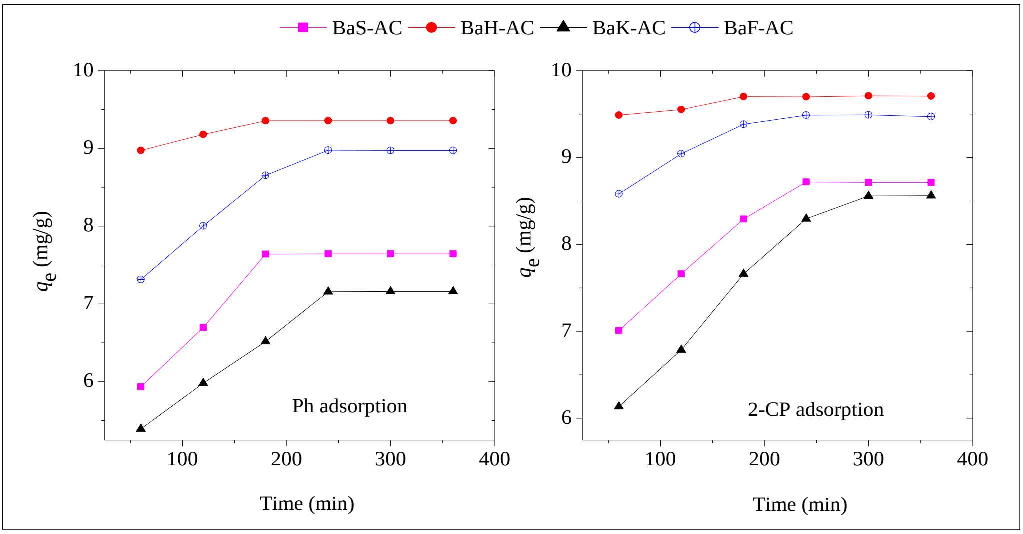

Figure 12: The plot of effect contact time on the adsorption capacity of Ph and 2-CP (Conditions: 28 °C, 50 mL of 100 mg/L Ph and 2-CP and 500 mg dose).

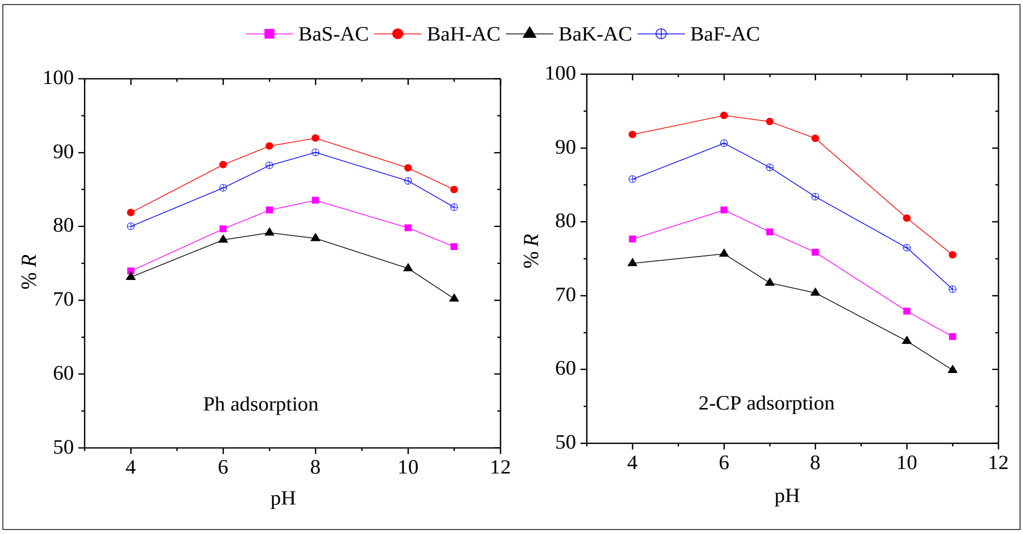

Figure 13: The plot of the effect of the adsorbate pH on the percentage removal of Ph and 2-CP (Conditions: 28 °C, 50 mL of 100 mg/L Ph and 2-CP, 500 mg dose and 6 hrs contact time).

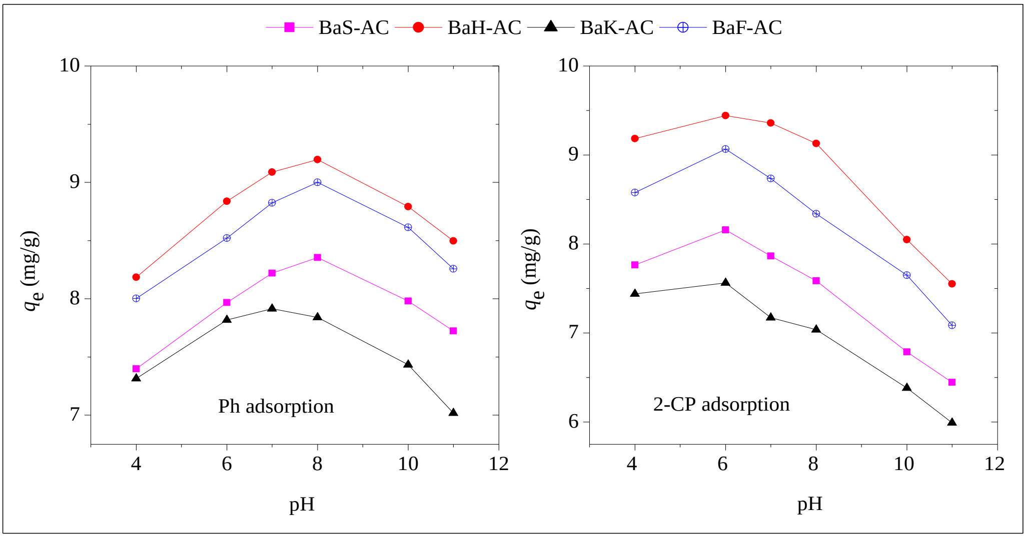

Figure 14: The plot of the effect of the adsorbate pH on the adsorption capacity of Ph and 2-CP (Conditions: 28 °C, 50 mL of 100 mg/L Ph and 2-CP, 500 mg dose and 6 hrs contact time).

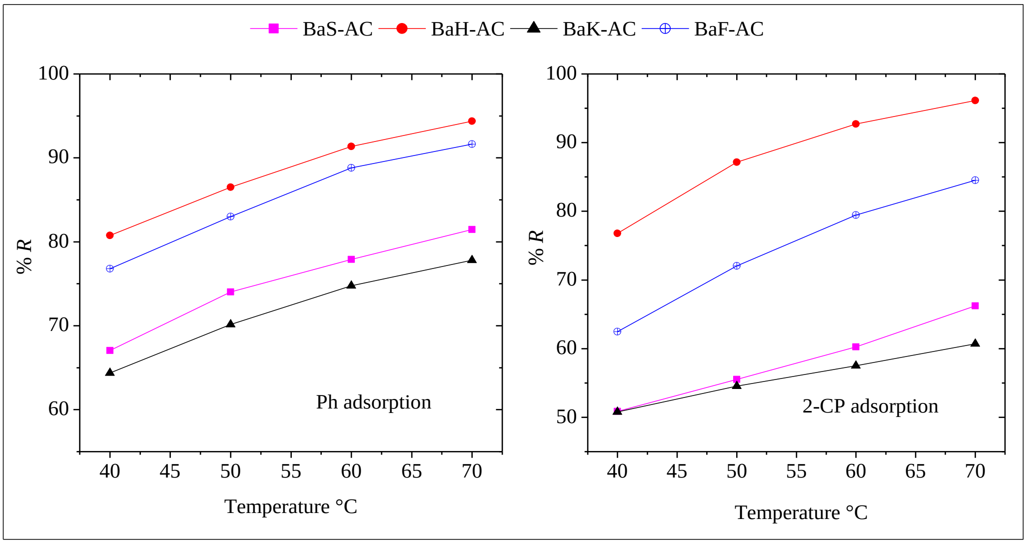

Figure 15: The plot of the effect of the batch solution temperature on the percentage removal of Ph and 2-CP (Conditions: 50 mL of 100 mg/L Ph and 2-CP initial concentration, 500 mg dose and 6 hrs contact time).

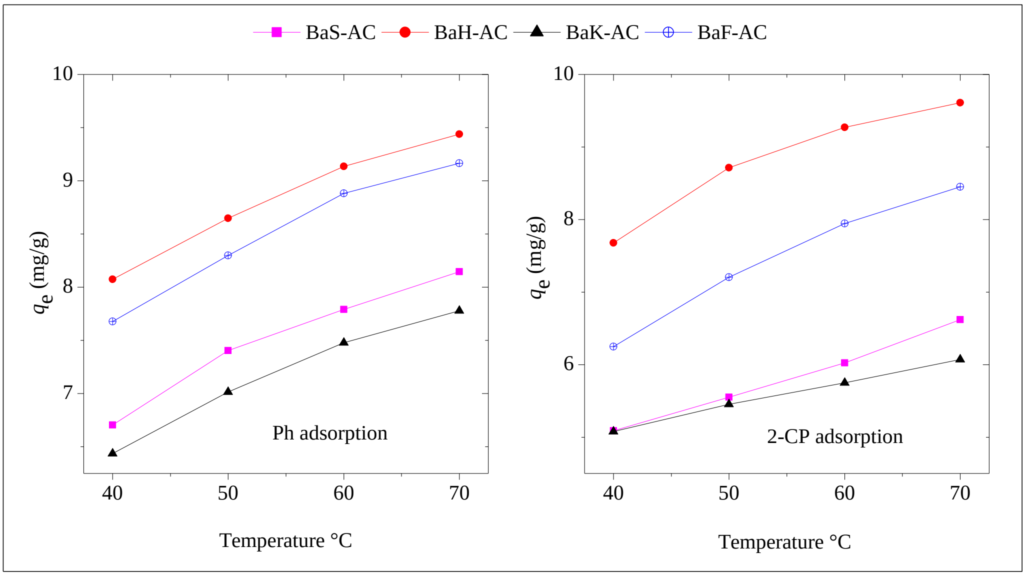

Figure 16: The plot of the effect of the batch solution temperature on the adsorption capacity of Ph and 2-CP using (Conditions: 50 mL of 100 mg/L Ph and 2-CP initial concentration, 500 mg dose and 6 hrs contact time).

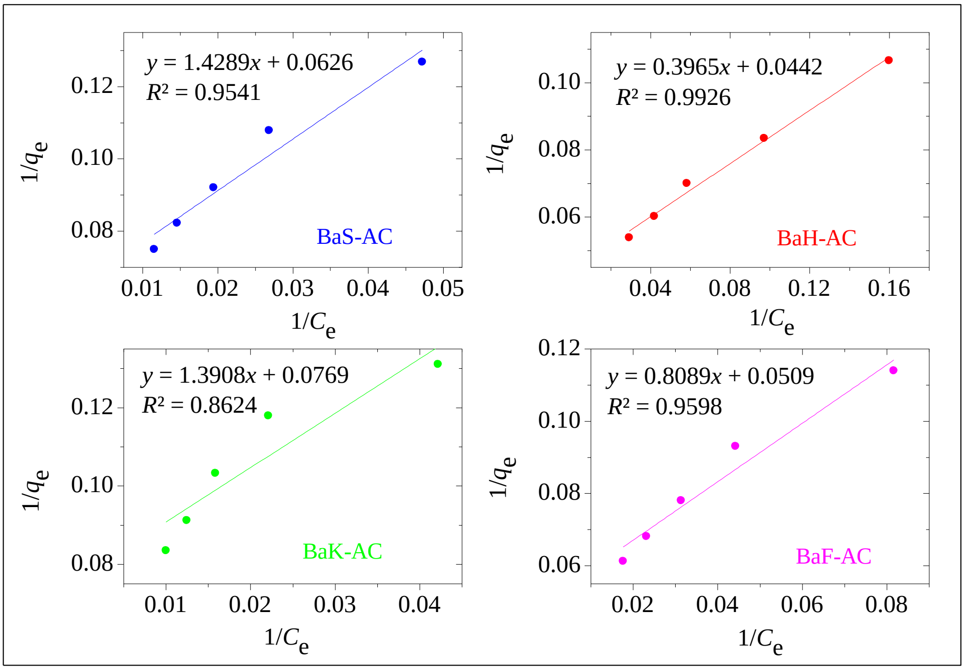

Figure 17 Combined Langmuir isotherm plot for the adsorption of Ph on BaS-AC, BaH-AC, BaK-AC and BaF-AC.

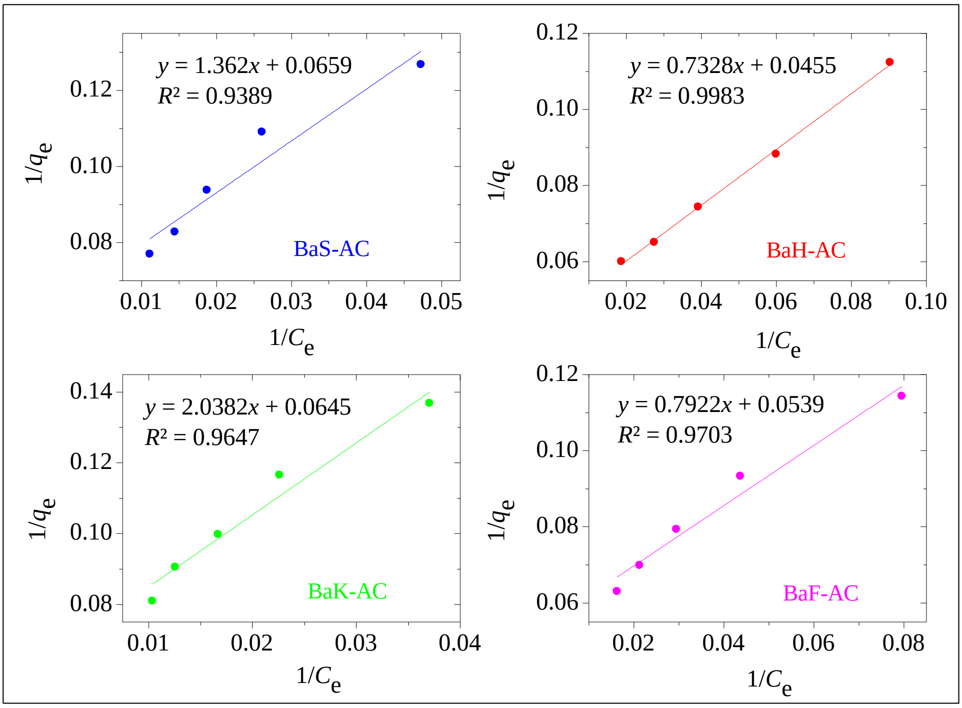

Figure 18: Combined Langmuir isotherm plot for the adsorption of 2-CP on BaS-AC, BaH-AC, BaK-AC and BaF-AC.

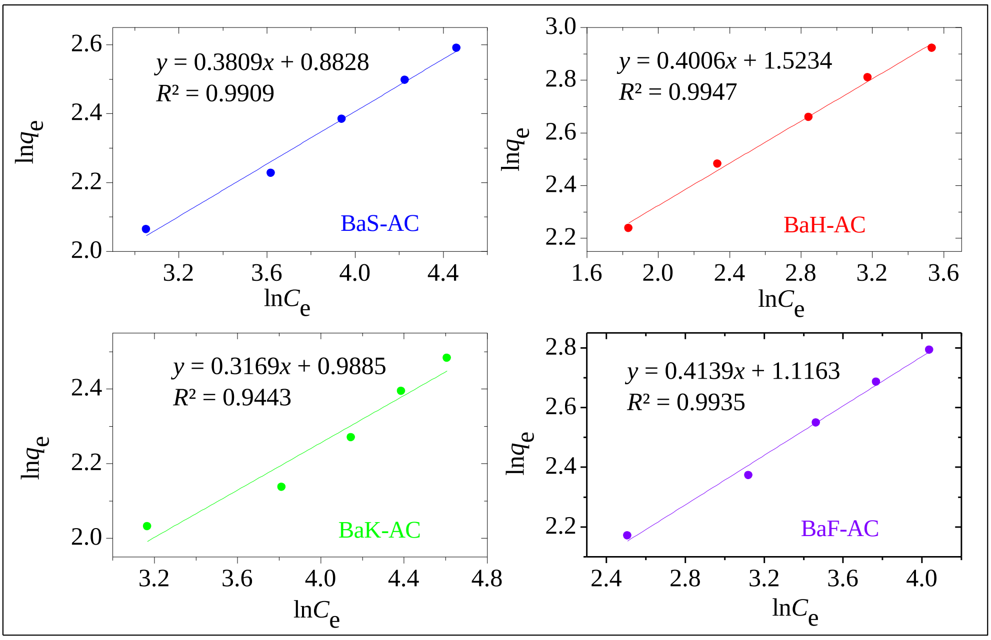

Figure 19: Combine Freundlich isotherm plot for the adsorption of Ph onto BaS-AC, BaH-AC, BaK-AC and BaF-AC.

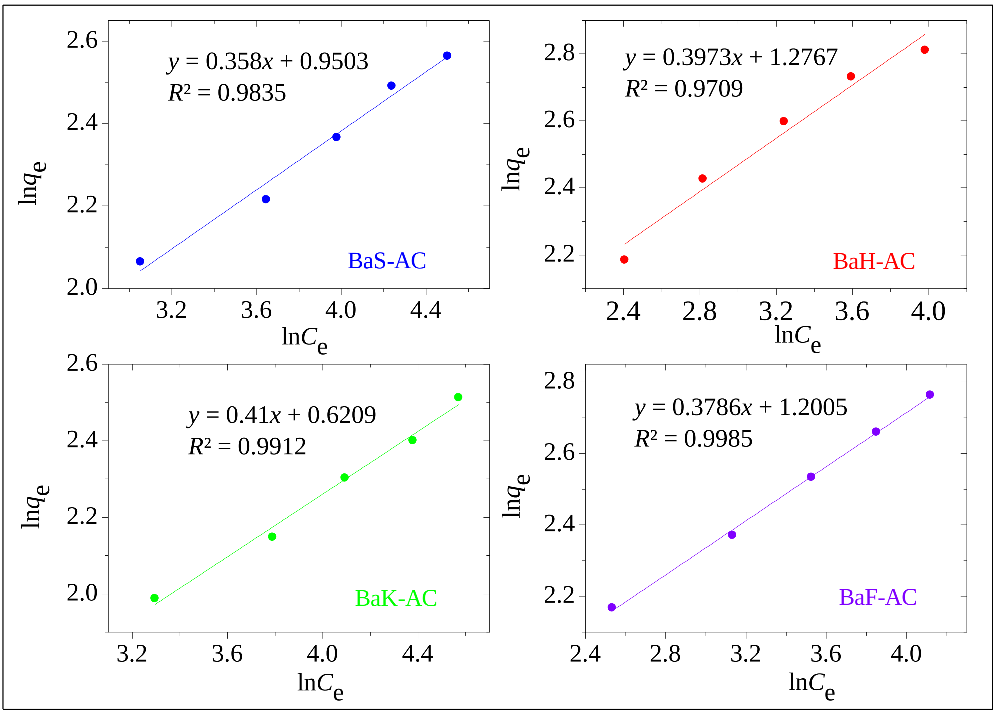

Figure 20: Combined Freundlich isotherm plot for the adsorption of 2-CP onto BaS-AC, BaH-AC, BaK-AC and BaF-AC.