Fabrication of high surface area acid-treated activated carbon from pomegranate husk for 2,4-dichlorophenol adsorption

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Abstract

In the present study, zinc chloride followed by acid treating was employed for fabrication activated carbon with a high surface area from pomegranate husk (APHAC) for 2,4-dichlorophenol (2,4-DCP) adsorption. The APHAC was a well-developed pore and exhibiting specific surface areas of $1576 \text{ m}^2/\text{g}$. Based on the XRD analysis, the diffraction peaks between 15° and 35° corresponded to amorphous carbon, and the pH_{pzc} values of APHAC was 6.15 ± 0.15 . According to batch experiments, the optimum adsorption condition of 2,4-DCP was pH of 3, contact time 60 min, and APHAC dose of 1.75. The absorption capacity of 2,4-DCP at the APHAC dose of 0.5 promptly decreased from $259.5 \pm 12.9 \text{ mg/g}$ at the initial concentration of 150 mg/L to $74.5 \pm 3.7 \text{ mg/g}$ dose of 2 g/L. With increasing temperature from 10°C to 50°C , the adsorption efficiency declined from $99.8 \pm 0.5\%$ to $75.6 \pm 1.89\%$. The isotherm and kinetic of 2,4-DCP by APHAC revealed that Freundlich and Elovich satisfactorily fitted with experimental data.

1. Introduction

One of the biggest concerns worldwide is water pollution. Phenolic compounds include many organic chemicals and are known as the most common water pollutants (Anisuzzaman et al. 2015). Industries such as pesticides, herbicides, plastics production, petroleum refineries, wood preservatives widely use chlorophenols (CPs). The CPs are often detected in surface water, landfill leachates, and industrial wastewaters (Okawa et al. 2004, Zou et al. 2009). 2,4-dichlorophenol (2,4-DCP) is a CPs that suspected to be endocrine disruptors and listed as one of the 65 priority pollutants by the US Environmental Protection Agency (Okawa et al. 2004). The 2,4-DCP widely used in pharmaceuticals and fungicides and has possessed great attention nowadays (Zhang et al. 2020). The 2,4-DCP is corrosive and can damage the kidneys, liver, lungs, skin, and digestive tract for humans, and it may also cause pathological symptoms (Pang et al. 2020). The 2,4-DCP has chlorine functional groups that make it a refractory compound in water resources and toxic for microorganisms because of chlorophenol's aromatic structure (Badu Latip et al. 2020). Due to the adverse of the 2,4-DCP on aquatic life and human health, its removal from water and wastewater is essential (Sadrnourmohamadia et al. 2017).

Some chemical and physical methods such as photocatalytic oxidation (Zhu et al. 2020), chemical oxidation (Sadrnourmohamadia et al. 2017), ion exchange (Nezamzadeh-Ejhieh & Ghanbari-Mobarakeh 2015), Fenton and electro-Fenton (Zhang et al. 2015), and biological degradation (Kargi & Eker 2005) have been studied for treating wastewater containing the 2,4-DCP. Some limitations for these methods are high-energy consumption, the lengthy-time required to produce excess sludge and secondary pollutants, and high cost (Badu Latip et al. 2020, Umar et al. 2010).

One of the frequently and effective methods for the phenolic compound's removal from aqueous solution is adsorption. The adsorption is a process based on the bulk of the solution's contact with a solid phase, which can adsorb the solutes dissolved in the solution phase selectively (Shaarani & Hameed 2010). One of the main drawbacks of applying activated carbon (AC) is AC's high price, limiting its application to a

full scale; thermally and chemically treated palm pith carbon, rice husk, and maize cob carbon have been used in the literature for 2,4-DCP removal (Akhtar et al. 2006). The type of activation processes, precursors, and thermal treatment procedures used in AC production can affect AC's existing functional groups responsible for adsorbing pollutants from solutions (Heidarinejad et al. 2020).

Therefore, this study aimed to synthesize high surface area acid-treated AC from pomegranate husk (APHAC) and investigate its performance toward the 2,4-DCP removal from aqueous media, optimizing the influencing parameters including the initial concentration of 2,4-DCP, the initial pH of the 2,4-DCP solution, APHAC dose, and contact time. Furthermore, to determine the adsorption mechanism, the isotherm adsorption, reaction kinetics, and ionic strength effect for 2,4-DCP removal using APHAC were explored.

2. Materials And Methods

2.1. Chemical and reagent

The 2,4-DCP (CAS 120-83-2, chemical formula $2,4-(\text{Cl})_2\text{C}_6\text{H}_3\text{OH}$) was purchased from Merck (Germany). During adsorption experiments, all the working solutions were prepared by dissolution of chemicals in deionized water.

2.2. Preparation of APHAC

The collected pomegranate husks (PHs) (Isfahan, Iran) were washed with tap water several times. The PHs were pulverized and sieved after drying for 12 h at 105 °C. The following procedure was used for APHAC fabrication: dissolve 100 g of ZnCl_2 in 50 mL of deionized water and add mixed with 100 g of PH, manually stirred under heating 70-80°C. The resulting paste was dried for 4 h at 105°C in a furnace, and afterward, the dried paste was transferred to the stainless-steel reactor and heated from room temperature to 600 °C at 10 °C/min for 30 min under the flux of N_2 (150 mL/min) (Leite et al. 2018, Lima et al. 2019b). After that, a 10.0 g of carbonized material and 200 mL of HCl (6 M) was placed in a 500 mL boiling flask; the mixture was stirred on a magnetic stirrer and reflux for 2 h at 70-80°C (Ribas et al. 2014, Thue et al. 2016). The slurry was cooled down and filtered, washed with deionized water several times, milled, sieved, and stored in an airtight container until use. The adsorbent was named acid-treated pomegranate husk activated carbon (APHAC).

2.3. Experiments of 2,4-DCP adsorption

The experiments of 2,4-DCP adsorption by APHAC were carried out in a batch system. The variables of the adsorption process including pH of the solution (3-9), APHAC dose (0.5-2 g/L), contact time (2-120 min), initial concentration of 2,4-DCP (50-150 mg/L), temperature (10-50 °C), and ionic strength (0.01-0.5 M) were investigated to determine the optimum adsorption conditions. The test solutions were mixed at 200 rpm to provide contact between APHAC particles and 2,4-DCP.

2.4. Analysis

The 2,4-DCP concentration in the solutions was quantified by a visible spectrophotometer (DR2000, Hach Company) at 510 nm. Eqs. (1) and (2) were employed for the calculation of adsorption efficiency and capacity.

See formulas 1 and 2 in the supplementary files.

Where %Removal and q are the removal percentage and sorption capacity, respectively, C_0 and C_f are, respectively, the influent and effluent concentrations (mg/L), V is the solution volume (L), and m is the sorbent mass (g).

3. Results And Discussion

3.1. Characteristics of APHAC

The values of specific surface area (S_{BET}) and total pore volume (V_{total}) were obtained from BET and BJH analysis (Fig. 1).

Fig. 1. N₂ adsorption and desorption isotherms, (inset) pore size distribution curve

The V_{total} and S_{BET} of APHAC were 0.83 cm³/g and 1576 m²/g, respectively, and confirmed a high surface area of APHAC. The high surface area of APHAC was mainly related to the application of ZnCl₂ and activating agent and acid leaching. Thue et al. (Thue et al. 2016) prepared the AC from wood chips by applying microwave and reported that S_{BET} of obtained AC decreased from 914.08 m²/g to 874.72 m²/g with increasing inorganic: organic ratio from 1:1 to 1:1.5. Also, Hadi et al. (Hadi et al. 2020b) fabricated AC from PH by dual chemical activation and reported that S_{BET} and V_{total} of AC were 811.12 m²/g and 0.404 cm³/g, respectively.

The XRD pattern of APHAC is displayed in Fig. 2.

Fig. 2. XRD pattern of APHAC

As illustrated, the broadbands ranging from 15° to 25° and 35° to 50° are corresponded to amorphous carbon and indicating that the acid leaching led to inorganic matter leaching from APHAC structure and prepared the carbon material with more amorphous pore walls, low crystallinity, and higher superficial area and pores structure. Similar results were reported by Ribas et al. (Ribas et al. 2014), who prepared AC from a cocoa shell with 6.0 M of HCl leaching for the reactive violet 5 dye removal from aqueous solutions and exhibited that amorphous carbon.

The FTIR spectrum of APHAC is illustrated in Fig. 3.

Fig. 3. The spectrum of FTIR of APHAC

As illustrated in Fig. 3, the band at 3432 cm^{-1} is ascribed to OH stretching (Thue et al. 2020), and the band at 2929 cm^{-1} was presumably related to the C-H vibrations in methyl and methylene groups (Baccar et al. 2009). The carboxylic acids or O=C stretching in esters was detected at 1637 cm^{-1} (Lima et al. 2019a). The band located at 1386 is ascribed to the -CH band (Umpierres et al. 2018). The C–O stretching of phenolic or carboxylate Groups cause a band’s emergence at 1023 cm^{-1} (Saucier et al. 2015). The vibrational band of C-H out-of-plane of aromatics presented two bands at 637 and 470 cm^{-1} .

The elemental analysis of precursor PH and APHAC are summarized in Table 1.

Table 1: Composition of precursor PH and APHAC

Material	Element (%)			
	C	H	N	S
Precursor PH	46.52	2.73	0.72	0.15
APHAC	83.23	0.89	2.02	0.13

As present in Table 1, the APHAC was comprised of C (83.23%), H (2.19%), N (2.02%), and S (0.13%) and demonstrating the synthesis of APHAC leads to increasing the C and N content due to pyrolysis of raw material and leaching processes. The higher C content of APHAC suggests that the predominant structure of APHAC is aromatic (Thue et al. 2020). A similar trend was reported by Hadi et al. (Hadi et al. 2020b), who investigated the fabrication of AC from PH by dual chemical activation and established that the C content of AC improved from 46.52 to 62.05% when converted to AC.

An SEM photograph of APHAC is shown in Fig. 4.

Fig. 4. SEM photo of APHAC

SEM micrograph of APHAC reveals rough surface morphology, and its surface shows an aggregate of several particles with a mean particle size of $74.4 \pm 6.3\text{ nm}$.

Fig. 5 presents the variation of pH_{PZC} by changing the APHAC dose.

Fig. 5. Variation of pH_{pzc} as function APHAC dose

As seen in Fig. 5, the pH_{pzc} values of APHAC were 6.17, 6.0, and 6.29 with the application of 0.1, 0.2, and 0.4 g/L, respectively. The various values of pH_{pzc} were reported in the literature (Hadi et al. 2020a, Hadi et al. 2020b, Ribas et al. 2014). Umpierres et al. (Umpierres et al. 2018) studied microwave application for AC preparation from tucumã seed and reported that the pH_{pzc} value was varied from 4.44 to 6.71. Ribas et al. (Ribas et al. 2014) reported that the value of pH_{pzc} was ranging from 2.35 to 7.31. The pH_{pzc} (Fig. 7) implies that at solution pH lower than 3.3, the APHAC has a positive surface charge, and higher than 3.3, the surface charge reverses to negative.

3.2. Adsorption of 2,4-DCP by APHAC

3.2.1. Effect of pH of the solution

To find performance adsorption of 2,4-DCP by APHAC under various solution pH, a series of the batch experiment were conducted at an initial 2,4-DCP concentration of 50 mg/L with different pH (Fig. 6).

Fig. 6. The removal performance of 2,4-DCP by APHAC under various pH (Concentration of 2,4-DCP: 50 mg/L, dose of APHAC: 0.5 and 0.75g/L, and contact time: 60 min)

As can be seen, with enhancing pH from 3 to 9, the performance of 2,4-DCP adsorption was reduced. When solution pH increased from 3 to 9, the performance of 2,4-DCP adsorption descended from $91.7 \pm 4.6\%$ to 73.5 ± 3.7 and from $93.3 \pm 4.7\%$ to 88.5 ± 4.4 with the application of 0.5 and 0.75 g/L of APHAC, respectively. As previously mentioned, the pK_a values of 2,4-DCP were 7.44 (Kuśmierik et al. 2016), and the obtained pH_{pzc} of APHAC was 6.15 ± 0.15 , and its surface is protonated form at pH values < 7.44 and negatively charged at pH values > 7.44 . The drop in the removal percentage for values of pH > 7.45 is explained by electrostatic repulsion of both negatively charged (adsorbent and adsorbate). On the other hand, there is a small decrease in removal from pH 3-7. The maximum adsorption occurs at pH 3, where the adsorbent is positively charged, and the adsorbate is presented in the protonated form. This circumstance demonstrates that the adsorption process's dominant mechanism was the interaction between the organophilic nature of the APHAC surface and undissociated OCs (Shaarani & Hameed 2010). Kalderis et al. (Kalderis et al. 2017) studied the 2,4-DCP adsorption by biochar and reported that the optimum solution pH was 2.

3.2.2. Effect of contact time and kinetic study

The contact time has a significant influence on the adsorption process. The variation of 2,4-DCP adsorption efficiency by APHAC was studied at contact time 2 to 120 min and displayed in Fig. 7.

Fig. 7. Variation of 2,4-DCP removal by APHAC as a function of contact time (2,4-DCP: 50-150 mg/L, solution pH: 3, dose of APHAC: 0.5 g/L, and contact time: 2-120 min)

As observed, overall, the 2,4-DCP adsorption efficiency enhanced with increasing contact time. At various studied initial 2,4-DCP concentration, the highest amount of the 2,4-DCP adsorption occurred within the first 15 min, and after 15 min the rate of adsorption was a slowdown and reached equilibrium at 60 min, and $92.9 \pm 1.9\%$, $87.2 \pm 1.7\%$, and $83.2 \pm 1.7\%$ of 2,4-DCP was adsorbed at 50, 100, and 150 mg/L of 2,4-DCP, respectively. With further growth of the contact time, the adsorption efficiency is almost unchanged. The initial rapid adsorption of 2,4-DCP may be attributed to specific active surface sites and functional groups in the adsorptive process (Mohan et al. 2007).

To realize the amount of 2,4-DCP removed from the aqueous solution based on the contact time, the study of kinetic adsorption is critical. In the present work, four frequent kinetic were studied. The studied kinetic equations are summarized in Supplementary Table S1. Fig. 8 shows the kinetic curves of 2,4-DCP

adsorption on APHAC at different initial 2,4-DCP concentrations, and the kinetic parameters are summarized in Table 2.

Fig. 8. Kinetic of 2,4-DCP adsorption by APHAC

Table 2: Constant of the kinetics of 2,4-DCP adsorption by APHAC

Kinetic models	Parameter	Initial 2,4-DCP concentration (mg/L)		
		50	100	150
Pseudo-first order	q_e (mg/g)	86.49 ± 2.65	163.2 ± 4.732	226.1 ± 10.33
	k_f (min ⁻¹)	0.3688 ± 0.0764	0.2386 ± 0.0404	0.2168 ± 0.0560
	R^2_{adj}	0.9139	0.9353	0.8494
Pseudo-second order	q_e (mg/g)	91.51 ± 1.92	175.4 ± 2.925	245.2 ± 9.048
	k_s (g/(mg.min))	0.0063 ± 0.0012	0.0021 ± 0.0002	0.0013 ± 0.0003
	R^2_{adj}	0.9717	0.9871	0.9359
Elovich	α (g/(mg.min))	1757.5 ± 811.5	556.4 ± 193.5	528.4 ± 177.9
	β (g/mg)	0.1034 ± 0.0064	0.0432 ± 0.0027	0.0292 ± 0.0019
	R^2_{adj}	0.9917	0.9871	0.9843
Avrami fractionary	q_e (mg/g)	101.73 ± 6.647	180.5 ± 5.093	372.4 ± 164.7
	k_{AV} (min ⁻¹)	0.2229 ± 0.0851	0.1703 ± 0.0236	0.0163 ± 0.045
	n_{AV}	0.2996 ± 0.0502	0.4403 ± 0.0432	0.2717 ± 0.0818
	R^2_{adj}	0.9931	0.9937	0.9845

As summarized in Table 2, all kinetic models can satisfactorily describe the 2,4-DCP adsorption data. However, based on the R^2_{adj} the Elovich and Avrami-fractional model were the best models. As can be seen, the value of q_e improved with increasing initial 2,4-DCP concentration.

3.2.2. Effect of APHAC dose and isotherm study

The adsorption of 2,4-DCP onto APHAC was measured at seven different doses of adsorbent at solution pH of 3 and contact time of 60 min and 50-150 mg /L of 2,4-DCP to investigate the influence of sorbent dose. The results of the adsorption experiments are shown in Fig. 9.

Fig. 9. (a) adsorption efficiency and (b) sorption capacity as function of APHAC dose (2,4-DCP: 50-150 mg/L, solution pH: 3, APHAC dose: 0.5-2.0 g/L, and contact time: 60 min)

It is clear that the adsorption performance of 2,3-DCP by APHAC was improved from $92.9 \pm 3.7\%$ to $99.8 \pm 0.5\%$, from $90.2 \pm 3.6\%$ to 99.1 ± 0.5 , and from 86.5 ± 3.5 to $99.3 \pm 0.5\%$ with increase in APHAC dose from 0.5 to 2.0 g/L for 50, 100, and 150 mg/L of 2,4-DCP, respectively. When the APHAC dose increased, the number of active sites for adsorption increased, and as a result, the higher amount of 2,4-DCP molecule can be adsorbed to the adsorption sites. The same trend is reported by others (Daware & Gogate 2020, Kalderis et al. 2017, Namasivayam & Kavitha 2005).

3.2.3. Effect of ionic strength

To investigate ionic strength's effect, the adsorption performance of 2,4-DCP dye onto APHAC was investigated at various ionic strengths (0.01-0.5M) and two constant doses of APHAC (1 and 1.75 g/L). The adsorption efficiency of 2,4-DCP as a function of ionic strength is given in Fig. 10.

Fig. 10. Performance removal of 2,4-DCP under various ionic strength (2,4-DCP: 50 mg/L, solution pH: 3, the dose of APHAC: 1 and 1.75, and contact time: 60 min)

As shown in Fig. 10, the APHAC adsorption performance declined from $98.2 \pm 0.3\%$ to $87.5 \pm 2.6\%$ and from $99.8 \pm 0.1\%$ to $95.5 \pm 2.9\%$ with application 1 and 1.75 g/L of APHAC when the ionic strength is changed from 0.01 to 0.5 M in the presence of salinity, two mechanisms can interfere on the adsorption process including compressing the double electric layer and leading to electrostatic repulsion of the sorbent molecules from the sorbate surface and the competition between the cationic ions and consequently dropping the surface electrostatic potential (Silva et al. 2020). Besides, the Na^+ ions can attract with π -electrons and lead to the formation of the positive electric layer, and as a result, the sorbent is surrounded by Cl^- ions, and then a diffuse layer of solvated ions is formed and lead to the reduction of adsorption performance (Bernal et al. 2020). As Bernal et al. (Bernal et al. 2020) mentioned, the adsorption performance reduction can be related to the increasing of Na^+ concentration and its competition with acetaminophen for the adsorption sites.

3.2.5. Adsorption temperature

To study the effect of temperature, the 2,4-DCP adsorption experiments by APHAC was performed at a temperature in the range of 10-50 °C (Fig. 11).

Fig. 11. Effect of temperature on APHAC adsorption performance (2,4-DCP concentration: 50, APHAC dose: 1.75, solution pH: 3, and contact time: 60 min)

As can be observed in Fig. 11, the adsorption efficiency of 2,4-DCP reduced with increasing temperature. The temperature increment from 10 to 50 °C led to a sharp decrease in adsorption efficiency from $99.8 \pm 0.5\%$ to $75.6 \pm 1.89\%$. Theoretically, when the solution's salinity is enhanced, the adsorption capacity is reduced due to the attractive electrostatic forces between adsorbate molecules and the adsorbent

surface. Conversely, when the ionic strength increased, the adsorption efficiency improved because of the repulsive electrostatic forces (Al-Degs et al. 2008). Hadi et al. (Hadi et al. 2020b) found that the adsorption of 4-chlorophenol declined from 75 to 33% with increasing ionic strength from 0 to 0.3 M.

3.2.6. Isotherm study

Here, three models, including Liu, Freundlich, and Langmuir model, were used to describe how 2,4-DCP interact with APHAC at two doses of APHAC (Supplementary Table S2). Fig. 12 displays the nonlinearized isotherms plot of 2,4-DCP using APHAC and obtained constants summarized in Table 3.

Fig. 12. Fitted isotherm of 2,4-DCP adsorption by APHAC

Table 3: Parameters of isotherm models

Model	Parameter	APHAC dose (g/L)	
		1	1.75
Freundlich	$K_F(\text{mg/g. (mg/L)}^{-1/n_F})$	34.29 ± 3.03	55.74 ± 3.89
	$1/n_F$	0.6259 ± 0.0651	0.4059 ± 0.1511
	R^2_{adj}	0.9954	0.9889
Langmuir	$Q_{max}(\text{mg/g})$	648.8 ± 62.12	256.9 ± 23.39
	$K_L(\text{L/mg})$	0.0277 ± 0.0046	0.1436 ± 0.0368
	R^2_{adj}	0.9913	0.9659
Liu	$Q_{max}(\text{mg/g})$	1774.8 ± 188.2	1215.2 ± 228.8
	$K_g(\text{L/mg})$	0.0034 ± 0.0021	0.0012 ± 0.0071
	n_L	0.7184 ± 0.1259	0.4588 ± 0.1137
	R^2_{adj}	0.9959	0.9875

Comparing to Langmuir and Liu isotherm, the highest R^2_{adj} are related to Freundlich isotherm and indicating a better fit. The Freundlich isotherm assumes that the adsorbate amount on the adsorbent surface increases as the adsorbate concentration increases (Bergmann & Machado 2015) and confirm the obtained data.

4. Conclusion

A high surface AC was prepared from PH using ZnCl_2 as a chemical activating agent and used for 2,4-DCP adsorption from the aqueous solution. The APHAC has a specific surface area of $1576 \text{ m}^2/\text{g}$, and the surface of APHAC was neutral at a pH value of 6.15 ± 0.15 . Batch experiments carried out on the APHAC-2,4-DCP sorption system indicated varied 2,4-DCP adsorption efficiency. The results showed that to decline the adsorption performance with increasing pH of the solution, initial 2,4-DCP concentration, and temperature. However, the adsorption efficiency of 2,4-DCP was further governed by the dose of APHAC. The APHAC-2,4-DCP interaction indicated a good fit with Elovich chemisorptions and the Freundlich isotherm. The isotherm, the Q_{max} , is very high for APHAC and is $648.8 \pm 62.1 \text{ mg/g}$ and $256.9 \pm 23.4 \text{ mg/g}$ with the application of 1 and 1.75 g of APHAC, respectively.

Declarations

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Ethical Approval

All procedures performed in study were in accordance with the ethical standards of the Iranian national research committee and its later amendments or comparable ethical standards.

Consent to Participate

The manuscript is an original work of all authors and all authors made a significant contribution to this study.

Consent to Publish

The authors hereby consent to publication of the work in Environmental Science and Pollution Research journal.

Authors Contributions

Ensiyeh Taheri: Investigation, Data curation, Formal analysis, Writing- Original draft preparation; **Mohammad Mehdi Amin:** Data curation, Writing- Original draft preparation; **Ali Fatehizadeh:** Conceptualization, Supervision, Methodology, Writing - Original draft preparation; **Eder C. Lima:** Software, Writing - Review & Editing.

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Competing Interests

The authors declare no conflict of interest

Availability of data and materials

Nil

References

- Akhtar M, Bhanger M, Iqbal S, Hasany SM (2006): Sorption potential of rice husk for the removal of 2, 4-dichlorophenol from aqueous solutions: Kinetic and thermodynamic investigations. *Journal of hazardous materials* 128, 44-52
- Al-Degs YS, El-Barghouthi MI, El-Sheikh AH, Walker GM (2008): Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon. *Dyes and pigments* 77, 16-23
- Anisuzzaman S, Joseph CG, Taufiq-Yap Y, Krishnaiah D, Tay V (2015): Modification of commercial activated carbon for the removal of 2, 4-dichlorophenol from simulated wastewater. *Journal of King Saud University-Science* 27, 318-330
- Baccar R, Bouzid J, Feki M, Montiel A (2009): Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions. *Journal of hazardous materials* 162, 1522-9
- Badu Latip NM, Gopal K, Suwaibatu M, Hashim NM, Rahim NY, Raoov M, Yahaya N, Mohamad Zain NN (2020): Removal of 2, 4-dichlorophenol from wastewater by an efficient adsorbent of magnetic activated carbon. *Separation Science and Technology*, 1-14
- Bergmann CP, Machado FM (2015): Carbon nanomaterials as adsorbents for environmental and biological applications. Springer
- Bernal V, Giraldo L, Moreno-Piraján JC (2020): Thermodynamic analysis of acetaminophen and salicylic acid adsorption onto granular activated carbon: Importance of chemical surface and effect of ionic strength. *Thermochimica Acta* 683, 178467
- Daware GB, Gogate PR (2020): Removal of pyridine using ultrasound assisted and conventional batch adsorption based on tea waste residue as biosorbent. *Environmental Technology & Innovation*, 101292
- Hadi S, Taheri E, Amin MM, Fatehizadeh A, Aminabhavi TM (2020a): Adsorption of 4-chlorophenol by magnetized activated carbon from pomegranate husk using dual stage chemical activation. *Chemosphere*, 128623
- Hadi S, Taheri E, Amin MM, Fatehizadeh A, Lima EC (2020b): Fabrication of activated carbon from pomegranate husk by dual consecutive chemical activation for 4-chlorophenol adsorption. *Environmental Science and Pollution Research*

- Heidarinejad Z, Dehghani MH, Heidari M, Javedan G, Ali I, Sillanpää M (2020): Methods for preparation and activation of activated carbon: a review. *Environmental Chemistry Letters*, 1-23
- Kalderis D, Kayan B, Akay S, Kulaksız E, Gözmen B (2017): Adsorption of 2,4-dichlorophenol on paper sludge/wheat husk biochar: Process optimization and comparison with biochars prepared from wood chips, sewage sludge and hog fuel/demolition waste. *Journal of Environmental Chemical Engineering* 5, 2222-2231
- Kargi F, Eker S (2005): Kinetics of 2, 4-dichlorophenol degradation by *Pseudomonas putida* CP1 in batch culture. *International biodeterioration & biodegradation* 55, 25-28
- Kuśmierek K, Szala M, Świątkowski A (2016): Adsorption of 2,4-dichlorophenol and 2,4-dichlorophenoxyacetic acid from aqueous solutions on carbonaceous materials obtained by combustion synthesis. *Journal of the Taiwan Institute of Chemical Engineers* 63, 371-378
- Leite AB, Saucier C, Lima EC, dos Reis GS, Umpierres CS, Mello BL, Shirmardi M, Dias SLP, Sampaio CH (2018): Activated carbons from avocado seed: optimisation and application for removal of several emerging organic compounds. *Environmental Science and Pollution Research* 25, 7647-7661
- Lima DR, Hosseini-Bandegharai A, Thue PS, Lima EC, de Albuquerque YRT, dos Reis GS, Umpierres CS, Dias SLP, Tran HN (2019a): Efficient acetaminophen removal from water and hospital effluents treatment by activated carbons derived from Brazil nutshells. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 583, 123966
- Lima DR, Lima EC, Umpierres CS, Thue PS, El-Chaghaby GA, da Silva RS, Pavan FA, Dias SLP, Biron C (2019b): Removal of amoxicillin from simulated hospital effluents by adsorption using activated carbons prepared from capsules of cashew of Para. *Environmental science and pollution research international* 26, 16396-16408
- Mohan SV, Ramanaiah S, Rajkumar B, Sarma P (2007): Biosorption of fluoride from aqueous phase onto algal *Spirogyra* IO1 and evaluation of adsorption kinetics. *Bioresource Technology* 98, 1006-1011
- Namasivayam C, Kavitha D (2005): Adsorptive removal of 2, 4-dichlorophenol from aqueous solution by low-cost carbon from an agricultural solid waste: coconut coir pith. *Separation Science and Technology* 39, 1407-1425
- Nezamzadeh-Ejhieh A, Ghanbari-Mobarakeh Z (2015): Heterogeneous photodegradation of 2, 4-dichlorophenol using FeO doped onto nano-particles of zeolite P. *Journal of Industrial and Engineering Chemistry* 21, 668-676
- Okawa K, Nakano Y, Nishijima W, Okada M (2004): Effects of humic substances on the decomposition of 2, 4-dichlorophenol by ozone after extraction from water into acetic acid through activated carbon. *Chemosphere* 57, 1231-1235

- Pang Y, Zhou Y, Luo K, Zhang Z, Yue R, Li X, Lei M (2020): Activation of persulfate by stability-enhanced magnetic graphene oxide for the removal of 2, 4-dichlorophenol. *Science of the Total Environment* 707, 135656
- Ribas MC, Adebayo MA, Prola LDT, Lima EC, Cataluña R, Feris LA, Puchana-Rosero MJ, Machado FM, Pavan FA, Calvete T (2014): Comparison of a homemade cocoa shell activated carbon with commercial activated carbon for the removal of reactive violet 5 dye from aqueous solutions. *Chemical Engineering Journal* 248, 315-326
- Sadrnourmohamadia M, Poormohammadib A, Almasic H, Asgarid G, Ahmadzadehe A, Seid-Mohammadid A (2017): Removal of 2, 4-dichlorophenol from aqueous solution using ultrasonic/H. *Desalination and water treatment* 75, 189-194
- Saucier C, Adebayo MA, Lima EC, Prola LDT, Thue PS, Umpierres CS, Puchana-Rosero MJ, Machado FM (2015): Comparison of a Homemade Bacuri Shell Activated Carbon With Carbon Nanotubes for Food Dye Removal. *CLEAN – Soil, Air, Water* 43, 1389-1400
- Shaarani FW, Hameed BH (2010): Batch adsorption of 2,4-dichlorophenol onto activated carbon derived from agricultural waste. *Desalination* 255, 159-164
- Silva CE^dF, Gama BM^Vd, Gonçalves AH^dS, Medeiros JA, Abud AK^dS (2020): Basic-dye adsorption in albedo residue: Effect of pH, contact time, temperature, dye concentration, biomass dosage, rotation and ionic strength. *Journal of King Saud University - Engineering Sciences* 32, 351-359
- Thue PS, Adebayo MA, Lima EC, Sieliechi JM, Machado FM, Dotto GL, Vaggetti JCP, Dias SLP (2016): Preparation, characterization and application of microwave-assisted activated carbons from wood chips for removal of phenol from aqueous solution. *Journal of Molecular Liquids* 223, 1067-1080
- Thue PS, Lima DR, Naushad M, Lima EC, de Albuquerque YRT, Dias SLP, Cunha MR, Dotto GL, de Brum IAS (2020): High removal of emerging contaminants from wastewater by activated carbons derived from the shell of cashew of Para. *Carbon Letters*
- Umar M, Aziz HA, Yusoff MS (2010): Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate. *Waste management* 30, 2113-2121
- Umpierres CS, Thue PS, Lima EC, Reis GS^d, de Brum IA, Alencar WS^d, Dias SL, Dotto GL (2018): Microwave-activated carbons from tucumã (*Astrocaryum aculeatum*) seed for efficient removal of 2-nitrophenol from aqueous solutions. *Environmental technology* 39, 1173-1187
- Zhang C, Zhou M, Ren G, Yu X, Ma L, Yang J, Yu F (2015): Heterogeneous electro-Fenton using modified iron-carbon as catalyst for 2, 4-dichlorophenol degradation: influence factors, mechanism and degradation pathway. *Water research* 70, 414-424

Zhang Q, He D, Li X, Feng W, Lyu C, Zhang Y (2020): Mechanism and performance of singlet oxygen dominated peroxymonosulfate activation on CoOOH nanoparticles for 2,4-dichlorophenol degradation in water. *Journal of hazardous materials* 384, 121350

Zhu Q, Sun Y, Xu S, Li Y, Lin X, Qin Y (2020): Rational design of 3D/2D In₂O₃ nanocube/ZnIn₂S₄ nanosheet heterojunction photocatalyst with large-area “high-speed channels” for photocatalytic oxidation of 2, 4-dichlorophenol under visible light. *Journal of hazardous materials* 382, 121098

Zou X, Wan X, Shi H, Wang D (2009): Adsorption of 2, 4-dichlorophenol from aqueous solution onto microwave modified activated carbon: Kinetics and equilibrium. *Transactions of Tianjin University* 15, 408

Figures

Figure 1

N₂ adsorption and desorption isotherms, (inset) pore size distribution curve

Figure 2

XRD pattern of APHAC

Figure 3

The spectrum of FTIR of APHAC

Figure 4

SEM photo of APHAC

Figure 5

Variation of pH_{pzc} as function MPHAC dose

Figure 6

The removal performance of 2,4-DCP by APHAC under various pH (Concentration of 2,4-DCP: 50 mg/L, dose of APHAC: 0.5 and 0.75g/L, and contact time: 60 min)

Figure 7

Variation of 2,4-DCP removal by APHAC as a function of contact time (2,4-DCP: 50-150 mg/L, solution pH: 3, dose of APHAC: 0.5 g/L, and contact time: 2-120 min)

Figure 8

Kinetic of 2,4-DCP adsorption by APHAC

Figure 9

(a) adsorption efficiency and (b) sorption capacity as function of APHAC dose (2,4-DCP: 50-150 mg/L, solution pH: 3, APHAC dose: 0.5-2.0 g/L, and contact time: 60 min)

Figure 10

Performance removal of 2,4-DCP under various ionic strength (2,4-DCP: 50 mg/L, solution pH: 3, the dose of APHAC: 1 and 1.75, and contact time: 60 min)

Figure 11

Effect of temperature on APHAC adsorption performance (2,4-DCP concentration: 50, APHAC dose:1.75, solution pH: 3, and contact time: 60 min)

Figure 12

Fitted isotherm of 2,4-DCP adsorption by APHAC

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