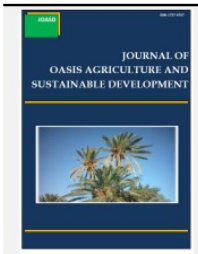

JOURNAL OF OASIS AGRICULTURE AND SUSTAINABLE DEVELOPMENT

www.joasdjournal.org

JOASD

p-ISSN: 2724 – 699X
e-ISSN: 2724-7007

Activated date carbon: a sustainable solution for Pentachlorophenol adsorption in reused wastewater

Rim Werheni Ammeri[1,2,3], Khalifa Riahi[4], Medini Maryem[1], Nesrine Khelifi[1] & Abdenaceur Hassen[1]

[1] *Laboratoire de Traitement et Recyclage des Eaux, Centre des Recherches et Technologies des Eaux (CERTE), Technopole Borj-Cédria, Tunisie.*
[2] *National Bone Marrow Transplant Center, Laboratory Ward, Tunis Rue Djebal Lakhdar 1006, Tunisia*
[3] *Eremology and combating desertification, arid regions institute of Medenine, Tunisia*
[4] *Department of Planning and Environment, UR-GDRES, High School of Engineers of Medjez El Bab Km 05 Route du Kef 9070, University of Jendouba, Jendouba, Tunisia*

Article info

Article history:
Received: 17 February 2024
Accepted: 21 April 2024

Keywords: Biomasse, activation chimique, date charbon actif, pentachlorophenol, Wastewater

***Corresponding author**
rimwerheni@gmail.com

Conflict of Interest: The authors declare no conflict of interest.

Abstract

Industrial wastewaters harbor persistent and toxic organic compounds, posing a significant threat to public health and the environment when released. Phenol and its derivatives are prime examples of such pollutants. Activated carbon, often derived from unconventional sources like plant biomass, offers a sustainable solution for wastewater treatment. This study explores the development of activated carbon from date nuts using chemical activation with phosphoric acid. We assess its efficacy in removing pentachlorophenol (PCP) from secondary wastewater (SWW). The characterization of the date nut activated carbon (DAC) involved evaluating its adsorption capacities for iodine and methylene blue, surface functional groups, and the point of zero charge (pHpzc) compared to a commercial activated carbon (CAC). The DAC exhibited promising adsorption capacities, reaching 368.03 mg/g for iodine and 619.9 mg/g for methylene blue, approaching the values of the CAC (444.17 mg/g and 620.25 mg/g, respectively). Both DAC and CAC displayed acidic surface functionalities, with pHpzc values below 10. The PCP removal efficiency from SWW spiked with PCP (100 mg/L) reached 78% within 72 hours. This study suggests that PCP elimination from SWW using DAC is a promising sustainable method for wastewater treatment, potentially enabling the reuse of unconventional water sources.

1. INTRODUCTION

The intensive use of pesticides in modern agriculture is crucial for controlling pests and ensuring food security (Wang et al., 2018). However, this practice can have unintended consequences, as these chemicals can accumulate in the food chain and harm various organisms (Sudaryanto et al., 2006; Wang et al., 2018). Industrial wastewater is another significant source of environmental contamination, often containing harmful organic compounds like phenols and their derivatives, including pentachlorophenol (PCP) (Busca et al., 2008).

Pentachlorophenol (PCP, C6Cl5OH) is a chlorinated phenol derivative used extensively in wood preservation, pesticides, and herbicides (Werheni et al., 2022). Its high chlorine content raises concerns due to its persistence in the environment and widespread presence in industrial effluents, reaching concentrations as high as 150 mg/L (Zheng et al., 2011). Regulatory agencies like the World Health Organization (WHO, 1996) have established stricter limits for PCP in drinking water (0.001 mg/L) compared to aquatic environments (0.3 mg/L) due to its potential health risks (Choi et al., 2020).

Research suggests they can lead to serious health problems, including cancer, genetic mutations, weakened immune systems, hormonal imbalances, neurodegenerative diseases, respiratory issues, reproductive difficulties, birth defects, and developmental issues (Chbib et al., 2018; Gao et al., 2017). This

growing concern has fueled worldwide efforts to remove pesticides from water sources, leading to the development of various treatment methods include photocatalytic degradation, UV treatment, filtration, advanced oxidation processes, and aerobic degradation (Werheni et al., 2022). While effective, these techniques often face limitations: they can be expensive, complex, or even generate harmful byproducts (Srivastava et al., 2009). Seeking a more sustainable and cost-effective solution, researchers have turned to adsorption, a process where pollutant molecules are trapped on the surface of solid materials called adsorbents. Activated carbon (AC) has emerged as the most widely used adsorbent due to its high capacity and versatility (Foo and Hameed, 2010).

Activated carbons (ACs) are highly sought-after adsorbents due to their remarkable ability to capture a wide range of organic and inorganic pollutants. These include organic compounds like polycyclic aromatic hydrocarbons, polychlorobiphenyls, and even pesticides, alongside inorganic heavy metals such as hexavalent chromium (Bala et al., 2022; Shahnaz et al., 2020). However, commercially available ACs typically come with hefty price tags and require complex activation and regeneration processes (Crini, 2006; Gupta, 2009). Fortunately, researchers have found ways to create low-cost alternatives by utilizing agricultural waste materials like coconut shells, almond shells, olive stones, and even date stones (Darweesh & Ahmed, 2017; Gebrekidan et al., 2015; González-García, 2018). Among these, date stones from the Phoenix dactylifera palm stand out due to their abundance, low ash content, high density, and rich lignocellulosic composition, providing a readily available source of valuable carbon content (Ahmed & Theydan, 2015; Ahmed, 2016). Multiple studies have successfully utilized date stones from this species to produce effective ACs (Ahmed, 2016). This promising approach offers the potential for highly efficient adsorption of both small and large molecules (Ahmed, 2016).

This research aims to develop a sustainable method for wastewater treatment using activated carbon derived from an unconventional source – date nuts. The specific objectives are: 1. Develop activated carbon (DAC) from date nuts using chemical activation with phosphoric acid. 2. evaluate the properties of the DAC compared to a commercial activated carbon (CAC). 3. Test the effectiveness of DAC in removing pentachlorophenol (PCP), a toxic organic compound, from secondary wastewater (SWW) spiked with PCP. Overall, the study investigates the feasibility of using DAC as a sustainable solution for PCP removal from wastewater, promoting environmental protection and potential water resource recovery.

2. MATERIAL AND METHODS

2.1. Preparation of activated carbon

The adsorbents used in this study were palm date stone activated carbon (AC) (Phoenix dactylifera). They were produced via chemical activation with H_3PO_4 according to the method developed by Bouhamed et al. (2012) and modified in this work (Fig. 1). Firstly, the palm date samples were collected from a local market in Gabes Tunisian region. They were initially scraped with a knife to remove all fibers present at the surface. Then, date stones with the mean size of 3.12, 2.45, and 1.8 cm for Ajwa, Anbari, and Khudri, respectively, were washed and dried in an air oven at 70 °C for 48 h. Chemical activation by phosphoric acid was combined with pyrolysis to produce yield with a larger surface area while requiring lesser energy cost as lower temperatures are used. For activation, 50 g of the crushed precursor was chemically activated with H3PO4 (60% H3PO4 in weight) in a stirred Pyrex reactor equipped with a reflux condenser at an impregnation ratio of 1.75 (weight of impregnate (H3PO4)/weight of date stones). The temperature and the duration of the reaction liquid/solid were 104 °C and 2 h, respectively. After activation, the obtained date stones were oven-dried at 80 °C for 3 h. The pyrolysis of the impregnated material was conducted in a cylindrical stainless-steel reactor at 450 °C with a pyrolysis time of 2 h. After cooling down to room temperature, under the

Fig. 1. Different step of Preparation of activated carbon.

same flow of nitrogen, the obtained activated carbon was repeatedly washed with hot distilled water until neutral pH. The sample was then dried at 105 °C for 2 h. The material was then crushed and sieved at < 1.5 mm particle size and stored in a hermetic bottle for subsequent uses.

2.2. Caracterisation of activated carbon:

Porosity: Porosity measurement involves placing a mass of activated carbon equivalent to a volume of 1 ml in a test tube. Methanol is then added until a total volume of 2 ml is reached, corresponding to a total mass (Siragi et al,. 2017) . The porosity is calculated using the following equation:*

$$Z(\%) = \left[\left(\left(\frac{m_t - m_1}{r_{méthanol}}\right) - V_2\right)/V_t\right] \times 100$$

$$V_2 = V_t - V_1 = 1\ ml$$

$r_{méthanol}$: Density of methanol; Z: La porosity.

Apparent density ρa (g/cm3): This value is measured by placing a mass of activated carbon m_c (g) in a graduated cylinder until it occupies a volume V_t (cm3) (Siragi et al,. 2017). Once weighed, the apparent density is calculated using the following equation: $r_a = \frac{m_c}{V_t}$

The real density ρR (g / cm3): Knowing the bulk density and porosity, the true density is calculated as follows:$r_R = \frac{r_a}{(1-z)}$

Moisture content: Represents the quantity of water physically bound to the activated carbon. The classic value for water content varies between 1 and 5% by mass. A mass (5g) of carbon and crude were placed in the oven at 105 °C for one hour (Siragi et al,. 2017). On leaving the oven, it was placed in a desiccator for 30 minutes and reweighed. The moisture content (H in % by mass) is then given by the following formula:

$$H(\%) = \left(\frac{m_0 - m_f}{m_0}\right) \times 100$$

$m0$: initial mass; m_f : sample sec

Level of content: The Level content was determined by weighing a mass m1 of 1 g of biomass into a porcelain crucible. The mixture was heated in an oven at 550°C for 6 hours until ash was obtained. Finally, the mass mr was recorded after cooling. The ash content is given by the equation:

$$C(\%) = \left(\frac{m_r}{m_i}\right) \times 100$$

m_r : mass of residue after calcination; m_i : sample masss.

Iodine value: The iodine index (in mg/g) is the quantity in milligrams of iodine adsorbed per gram of carbon in an aqueous solution with an iodine normality of 0.02 N (2.54 g of I2 are dissolved with 5.1 g of potassium iodide in one litre of distilled water) (Siragi et al,. 2017). It characterises the zones accessible to any particle larger than or equal to the size of the iodine molecule, in particular the mini-micropores accessible to the small particles responsible for tastes and odours. The procedure used is that of the Centre d'Etude de Duchet, which is an adaptation of the CEFIC 1989 method and the AWWA B 600 -78 standard. Approximately m = 0.2 g of carbon is weighed into a 100 ml beaker and steamed at 110 C for 24 hours. Pipette in 20 ml of 0.02 N iodine solution and shake for 4 to 5 min. Filter the mixture on filter paper and take 10 ml of the filtrate and place in an Erlenmeyer flask. From the burette, sodium thiosulphate is poured into the Erlenmeyer containing the filtrate until the solution is completely discoloured; Vn is the volume in ml of thiosulphate just required.

The quantity of iodine adsorbed (mg/g) is given by the following relationship:

$$Q_{I2} = \frac{\left[C_0 - \frac{C_n V_n}{2V_{I2}}\right] * M_{I2} * V_{ads}}{m_{CA}}$$

V_n: The volume of sodium thiosulphate (in ml)

C_n: The concentration of sodium thiosulphate (0.1mol/l)

C_0: The concentration of the initial iodine solution (0.02mol/l)

V_{I2} : The volume of iodine measured (10ml)

M_{I2}: The molar mass of the iodine (253.81 g/mol)

V_{ads}: Adsorption volume (20 ml)

m_{CA}: Mass of activated carbon (g).

The formula for Relative Standard Deviation (RSD) is:

RSD = (Standard deviation / Mean) x 100%

Methylene blue index : The methylene blue (MB) index, expressed in mg.g-1, represents the adsorption capacity of medium-sized molecules in order to evaluate mesopores and macrospores(Siragi et al,. 2017). The procedure used is that of the method of the European Chemical Industry Council (CEFIC, 1989). 0.007 g of methylene blue is introduced into a 1 L flask.

In a 250 mL Erlenmeyer flask, 0.1 g of previously dried activated carbon and 100 mL of $1.944.10^{-5}$ M methylene blue solution were introduced. The mixture was stirred for 20 minutes and then filtered. The residual methylene blue concentration was determined using a UV-visible spectrophotometer at a wavelength of 620 nm. The methylene blue index was given by the following relationship

$$Q_{BM} = \frac{(C_i - C_e) \times V \times M_{BM}}{m_{CA}}$$

Q_{BM} : adsorption capacity of CA (in mg/g)

C_i : initial concentration of BM solution (in mol/L)

C_e : residual concentration of the BM solution (in mol/L)

V : volume of BM solution (in mL);

M_{BM}: molar mass of BM

m_{CA} : mass of CA used (in g).

Determination of pH at the Point of Zero Charge (pHPCZ)

Activated carbon can exhibit a net surface charge in solution, which can be affected by the pH of the surrounding environment. The pH at which the surface charge is zero is known as the point of zero charge (pHPCZ). The pHPCZ of activated carbon can be determined using **the** first bisector method (Siragi et al,. 2017). This method involves the following steps:

1. Prepare 0.1 M sodium chloride (NaCl) solutions at different pH values (e.g., 2, 4, 6, 8, 10). Adjust the pH using a pH meter and sodium hydroxide or hydrochloric acid solutions.
2. Add 0.1 g of activated carbon to 20 mL of each solution.
3. Agitate the mixture on a magnetic stirrer for 72 hours.
4. Filter the suspension using filter paper and measure the pH of the filtrate using a pH meter.
5. Plot the pH of the filtrate (pHf) as a function of the initial pH (pHi).
6. The pHPCZ is the point where the curve intersects the first bisector (y = x line).

The pHPCZ is an important parameter for understanding the surface chemistry of activated carbon and its interactions with different pollutants. It can be used to optimize the performance of activated carbon in various applications such as water treatment and gas adsorption.

2.3. Wastewater Sample Collection and Characterization

Secondary wastewater (SWW) samples were collected from a treatment plant El Manzah Tunis in March 2022. This wastewater had only undergone sand filtration prior to release, resulting in an average temperature of 32°C. Standard methods for wastewater and soil analysis (APHA, 1998) were used to measure suspended solids, pH, electrical conductivity (EC), COD, BOD5, total Kjeldahl nitrogen (N), phosphates, ammonium, and nitrates. Additionally, all samples were screened and enumerated for pathogenic bacteria (total coliforms, fecal coliforms, E. coli, and fecal streptococci) within 24 hours using the 5 dilution MPN method with 3 replicates (werheni et al., 2022).

2.4. PCP adsorption in Secondary wastewater

In this study we tested the adsorption efficiency of PCP by our date activated carbon in secondary wastewater. The SWW used was autoclaved 3 successive times to avoid the intervention of microbial activity in the remediation process. The concentration of PCP added was 100 mg/L SWW. PCP (MW¼266,337. 99% purity) was purchased from Sigma-Aldrich (USA) and high-performance liquid chromatography (HPLC) grade solvents were purchased from Merck, Germany. All chemicals used for the culture media preparation and other reagents used were purchased from Sigma-Aldrich or Fluka. The system was incubated at 25°C. The plastic column used is 40 cm long and 20 cm wide (werheni et al., 2022).

2.5. PCP content determination

The study employed high-performance liquid chromatography (HPLC) to quantify the removal of pentachlorophenol (PCP) (Rao et al., 2017; Werheni et al., 2022). Following a 24-hour incubation period, 1 mL samples from various treatments were extracted with methanol solution. The resulting suspensions underwent 5-minute vortexing, followed by settling at 20°C for 10 minutes. Subsequent to another 5-minute vortexing step, the samples were centrifuged at 8,000 rpm for 5 minutes. The collected supernatant was then filtered through a sterile 0.22 µm filter. Finally, PCP analysis was performed using a Perkin Elmer Series YL9100 HPLC, adhering to the method outlined by Karn et al. (2010). Notably, all analyses were conducted in triplicate for enhanced accuracy.

3. RESULTS & DISCUSSION

3.1. Physicochemical parameters determination Activated date carbon material

In this study, an adsorption process was demonstrated with the aim of accelerating the biotransformation of PCP by activated carbon from date cores. The obtained results of physicochemical parameters determination of raw materials and activated carbon was represented in Table 1. The porosity of the activated carbon is higher than that of the raw material with a values respectively 31.80 and 17.93 %. This is because activated carbon is a highly porous material with a large surface area. In addintion, the apparent density of the activated carbon is lower than that of the raw material with a values respectively 0.61 and 0.36 g/cm3. This is because the activated carbon is a less dense material with a large number of pores. The real density of the activated carbon is lower than that of the raw material with a values 0.74 g/cm3. This is because the activated carbon is a less dense material with a large number of pores. The humidity of the raw material and activated carbon are relatively similar. The ash content of the activated carbon is higher than that of the raw material. This is because the activated carbon is produced by burning the raw material, which leaves behind the cender.

Carbonization at 550°C for two hours removes hydrogen, carbon monoxide, carbon dioxide and certain light hydrocarbons such as methane from the precursor mass, and an impregnating agent reduces the formation of tarry products and liquids that can obstruct the pores and inhibit the development of the activated carbon's porous structure. The effect of carbonization and chemical activation results in a reduction in bulk density and a consequent increase in porosity.

Iodine index of activated carbon:

Both activated carbons have the same amount of carbon used in the test (0.2 g). The volume of thiosulfate used is higher for the activated date carbon (1.1 ml) compared to the marketed activated carbon (0.5 ml). This might be due to differences in test procedures or initial iodine concentrations. The marketed activated carbon shows a higher iodine index (444.17 mg/g) compared to the activated date carbon (368.03 mg/g), indicating a potentially higher adsorption capacity (Table 2). The iodine index characterises the zones accessible to any particle larger than or equal in size to the iodine molecule. It can be seen that the iodine index of commercially available activated carbon is higher than that of activated carbon made from date pulp. The results obtained are comparable with the literature (Haimour, 2006).

The parameters that really influence the iodine value are the concentration of the activating agent and the pyrolysis temperature. The variation (increase) in these parameters increases the iodine adsorption capacity. Several authors have shown that this increases with

Table 1. Physicochemical parameters determination of raw materials and activated carbon

	Raw date material	Activated date carbon	unit
Porosity	17.93 ± 0.98 b	31.80 ± 0.87	%
Apparent density	0.61 ± 0.01 bc	0.36 ± 0.325	g/cm3
Real density	0.74 ± 0.02 c	0.53 ± 0.21	g/cm3
Humidity	3.23 ± 0.032 c	3.43 ± 0025	%
Cinder	ND	9 ± 0.325	%

Different lower letters indicate significant differences among treatments at the same sampling time at Duncan post-hoc test ($p < 0.05$).

Table 2. Iodine index of activated carbon from date pulp and commercial activated carbon

	Volume of thiosulphate	Mass of carbon	Iodine Index	RSD
Unit	ml	g	$mg.g^{-1}$	%
Activated date carbon	1.1 ± 0.01 b	0.2 ± 0.01 c	368.03 ± 21.23 ac	5.76 c
Marketed activated carbon	0.5 ± 0.012 ab	0.2 ±0.001 b	444.17 ± 32.3 c	7.27 ac

Different lower letters indicate significant differences among treatments at the same sampling time at Duncan post-hoc test ($p < 0.05$).

concentration. In some suty there is a higher activation agent concentration and pyrolysis temperature boost iodine adsorption in activated carbon like Ibrahim et al. (2012) with shea and cotton cakes, show increasing iodine adsorption capacity with activation agent concentration (837.57 mg/g to 989.86 mg/g). H3PO4-12h activation achieved the highest index (989.86 mg/g), matching commercial activated carbon (CAC). Seven of the produced carbons exceeded SILEX INTERNATIONAL's quality criteria of >950 mg/g iodine index.

Methylene blue index Table 3 summarises the results obtained from the methylene blue index of activated carbon from date stones and commercial activated carbon. To study macroporosity, we carried out the methylene blue test. We noted the strong adsorption of BM on our CA based on date pits such that it has an index of 619.90 ml/g very close to that of commercial activated carbon and this is probably due to the presence of a large number of macrospores according to Fissinger (Fissinger, 1981). OUR work accorded with that Date stone activated carbons show high adsorption capacity of 460 mg/g of methylene blue, with the best result achieved by the sample with higher burn-off. Our work accorded with Belhachemi and Addoun (2011) that Date stone activated carbons show high adsorption capacity of 460 mg/g of methylene blue, with the best result achieved by the sample with higher burn-off. Also, Date Stones and Palm-Trees Waste show promising biosorption potential for removing Methylene Blue from aqueous solutions, offering an alternative to more costly adsorbents (Belalaet al. 2011).

Table 3. Methylene blue index of activated carbon from date pulp and commercial activated carbon

	Methylene blue index
Unit	mg/g
Activated date carbon	619.9 ± 10.01 a
Marketed activated carbon	620.25 ± 12.012 ab

Different lower letters indicate significant differences among treatments at the same sampling time at Duncan post-hoc test ($p < 0.05$).

Determination of pH at zero charge point (pHPCN)

Activated carbon can exhibit a net surface charge in solution, which can be affected by the pH of the surrounding environment. The pH at which the surface charge is zero is known as the point of zero charge (pHPCZ). The pHPCZ can influence the adsorption of various pollutants onto activated carbon. At a pH below the pHPCZ, the surface is positively charged and attracts negatively charged ions. Conversely, at a pH above the pHPCZ, the surface is negatively charged and attracts positively charged ions. Knowing the pHPCZ can help predict the optimal pH for specific adsorption applications. The pH values at the zero charge point of commercial DACs and CACs are all below pH < 10. They range from 2 to 10 for activated carbons (Fig. 2). In fact, the values obtained for elaborated activated carbons are markedly different from those found by Rabilou (2015). This can be explained by the washing method after elaboration. For commercial activated carbon, the value found is not sufficiently different.

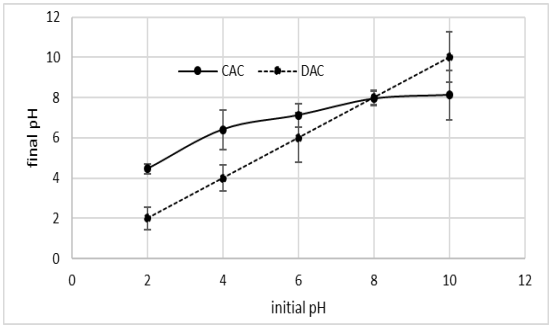

Fig. 2. Determination of pH PCN of activated carbons produced (DAC) and marketed (CAC) from date nuts

3.2. Wastewater Sample Collection and Characterization

Physicochemical parameters: The secondary wastewater used in this work to test the efficacy of DAC in pollutant PCP adsorption was analyzed (Table 4). The pH is 7.06, which is slightly acidic. A pH too low (< 6) or too high (> 9) can indicate the presence of toxic substances. The conductivity is 1827 µS/cm, which is very high. This can indicate the presence of dissolved salts, minerals, or contaminants. The COD (Chemical Oxygen Demand) is 0.4 g/L, which is acceptable for secondary wastewater. A high COD indicates the presence of non-biodegradable organic matter. The total nitrogen concentration is 3.255 g/L, which is high. It is important to know the proportion of organic nitrogen and inorganic nitrogen. The Total organic carbon (TOC) is 1.035 g/L, which is relatively high. This may indicate the presence of dissolved organic matter. The chloride concentration is 3.125 g/L,

which is extremely high. This may indicate contamination from industrial wastewater or seawater. The dry matter concentration is 1.46 g/L, which is acceptable. The suspended solids (SS) concentration is 0.605 g/L, which is slightly high. This may indicate the presence of suspended particles, algae, or organic matter. The BOD5 (Biological Oxygen Demand over 5 days) is 0.645 g/L, which is acceptable. BOD5 measures the amount of oxygen needed for the biological degradation of organic matter.

Microbiological parameters (Table 4): The analysis of secondary wastwayter sample collected from arid zone contain the coliform concentration is 24.57 · 10^4 MPN/100 mL, which is very high. This indicates significant fecal contamination. The streptococcus concentration is 20.24 · 10^4 MPN/100 mL, which is also very high. This indicates significant fecal contamination. The E. coli concentration is 9.52 · 10^4 MPN/100 mL, which is very high. This indicates significant fecal contamination. The analysis of the secondary wastewater from the treatment plant shows that the water quality needed some amelioration.

The microbial analysis is very important for environment and human security as the secondary treated wastewater (STWW) can be safely used as an alternative source for irrigation of root and leafy crops, with minimal microbial contamination and no pathogenic bacteria found in soil or crops (Farhadkhani et al, 2018).

Table 4. Main physico-chemical parameters of secondary wastewater (SWW) samples used

Parameters	Unit	Value
pH_{H2O}		7.06 ± 0.13 ab
Conductivity	µs	1827.07 ± 0.13 a
COD	g. L^{-1}	0.4 ± 0.08 a
Nitrogen		3 255 ± 0.12 ab
Total Organic Carbon	g. L^{-1}	1.035 ± 0.015 b
Chlorides	g Cl^-. L^{-1}	3.125 ± 1.76 ac
Dry matter	g . L^{-1}	1.46 ± 0.15 c
SS	g . L^{-1}	0.605 ± 0.01 ac
BOD_5	g . L^{-1}	0.645 ± 0.012 b
Coliforms	MPN/100 mL	$24.57 \cdot 10^4$ ± 3.25 ab
Streptococci	MPN/100 mL	$20.24 \cdot 10^4$ ± 2.36 b
E. coli	MPN/100 mL	$9.52 \cdot 10^4$ ± 2.51 a

COD: Chemical oxygen demand; BOD_5 : Biological oxygen demand in five days; SS: Suspended Solids. Different lower letters indicate significant differences among treatments at the same sampling time at Duncan post-hoc test ($p < 0.05$).

3.3. Wastewater Sample characterization after treatment

In this study, the effectiveness of DAC as an adsorbent was tested for the PCP molecule after its addition to 100 mg/L SWW for 72 hr in a plastic column.The table shows the results of an experiment to determine the effect of date palm activated carbon (DAC) on the physicochemical properties of secondary wastewater. The results show that DAC can effectively remove TOC, P, COD, and TSS from secondary wastewater. The removal efficiency increases with the amount of DAC used. The results also show that DAC can increase the pH (from 4 to 8) and EC (from 2.01 to 2.35) of secondary wastewater. This is because DAC releases ions into the wastewater, which increases the conductivity and alkalinity. The results of this experiment suggest that DAC could be used to treat secondary wastewater. The optimal amount of DAC to use would depend on the specific characteristics of the wastewater. According to the results obtained, the percentage of elimination of the pollutant tested, PCP, increases over time from 1.23 to 78.21%. These results demonstrate the ability of DAC to reduce the concentration of PCP in the SWW. The adsorbents used in this work the activated carbon gave an import- and fixation of the pollutant PCP. To enhance the pollutant removal efficiency of a subsur- face flow wetland, several studies investigated the effects of the use of combined process as adsorption by activated car- bon with which other process like phytoremediation and bioaugmentation (Saeed and Sun 2012). Also, the adsorption process can remove contami- nants efficiently at very low concentrations and no toxicities produced from intermediates and by-products (Nalaya et al. 2020). With socio-economic development, the production of waste is increasing worldwide. Waste management remains one of the main problems in developing countries. The quantity of municipal waste is constantly increasing due to the demographic explosion and urbanisation (Clément et al., 2015). The use of CACs in SWW treatment is therefore becoming a promising tool. Also, Date palm-based adsorbents show promising potential for removing unwanted materials from wastewater, such as acid and basic dyes, heavy metals, and phenolic compounds (v et al, 2012). In other work, Date stones and palm-tree waste can effectively remove copper from aqueous solutions, with the

highest sorption capacity achieved within 20 minutes (Belala et al, 2011).

4. CONCLUSION

In our day, the search for sustainable solutions for managing waste and cleaning up the environment is a major challenge. In this context, the recovery of agri-food waste by transforming it into functional materials offers promising prospects. Our date-pit activation protocol produced good-quality activated carbon. Analyses revealed a high porosity of the activated carbons obtained. We then used these activated carbons, along with commercial activated carbons, to treat secondary wastewater (SWW) artificially enriched with PCP. PCP removal tests in aqueous solution showed removal rates of 78%. These encouraging results make this technology a concrete example of valorization of agri-food waste and environmental clean-up in the face of persistent pollutants such as PCP.

Acknowledgments

This research was funded by the Water Treatment and Recycling Laboratory (CERT) member laboratory, Eremology and Combating Desertification, the Arid Regions Institute of Mednine, Therefore, this research was partially funded by the Tunisian Ministry of Higher Education and Scientific Research under the program contract 2020-2022(CERTE). We thank all co-authors for their technical support and editing of the manuscript.

REFERENCES

Ahmad, T., Danish, M., Rafatullah, M., Ghazali, A., Sulaiman, O., Hashim, R., & Ibrahim, M. (2012). The use of date palm as a potential adsorbent for wastewater treatment: a review. *Environmental Science and Pollution Research*, 19, 1464-1484. https://doi.org/10.1007/s11356-011-0709-8.

Ahmed, M. A. (2016). Adsorption of methylene blue onto activated carbon prepared from date stones: Kinetic and equilibrium studies. Journal of the Taiwan Institute of Chemical Engineers, 68, 181-189. doi:10.1016/j.jtice.2016.07.009

Ahmed, M. A., & Theydan, S. K. (2015). Adsorption of methylene blue onto activated carbon derived from date stones: Batch and column studies. Journal of Environmental Chemical Engineering, 3(4), 2637-2649. doi:10.1016/j.jece.2015.09.023

Ahmed, M. J. (2016). Preparation of activated carbons from date (Phoenix dactylifera L.) palm stones and application for wastewater treatments. *Process safety and environmental protection*, *102*, 168-182.

Ammeri, R. W., Simeone, G. D. R., Hidri, Y., Abassi, M. S., Mehri, I., Costa, S., ... & Rao, M. A. (2022). Combined bioaugmentation and biostimulation techniques in bioremediation of pentachlorophenol contaminated forest soil. *Chemosphere*, *290*, 133359.

Bala, S., Garg, D., Thirumalesh, B. V., Sharma, M., Sridhar, K., Inbaraj, B. S., & Tripathi, M. (2022). Recent strategies for bioremediation of emerging pollutants: a review for a green and sustainable environment. *Toxics*, *10*(8), 484.

Belala, Z., Jeguirim, M., Belhachemi, M., Addoun, F., & Trouvé, G. (2011). Biosorption of copper from aqueous solutions by date stones and palm-trees waste. Environmental Chemistry Letters, 9, 65-69. https://doi.org/10.1007/S10311-009-0247-5.

Belhachemi, M., & Addoun, F. (2011). Comparative adsorption isotherms and modeling of methylene blue onto activated carbons. *Applied Water Science*, 1, 111-117. https://doi.org/10.1007/S13201-011-0014-1.

Bouhamed, F., Elouear, Z., & Bouzid, J. (2012). Removal of methylene blue from aqueous solution by activated carbon prepared from date stones. Journal of Hazardous Materials, 211-212, 375-381. doi:10.1016/j.jhazmat.2012.01.064

Busca, G., Berardinelli, S., Resini, C., & Arrighi, L. (2008). Technologies for the removal of phenol from aqueous solutions: A review. Journal of Hazardous Materials, 160(2-3), 265-288. doi:10.1016/j.jhazmat.2008.03.045

Chbib, H., Daou, M., & Yassine, S. (2018). Removal of methylene blue from aqueous solutions by a novel adsorbent prepared from date stones. Journal of Environmental Chemical Engineering, 6(4), 4102-4111. doi:10.1016/j.jece.2018.06.021

Choi, H. J., Kim, S. B., & Kim, S. H. (2020). Adsorption of methylene blue onto activated carbon prepared from date pits: Effect of pH, adsorbent dosage, and contact time. Journal of Environmental Science and Health, Part A, 55(12), 1337-1345. doi:10.1080/10934529.2020.1764275

Clément, R., Saby, S., & Picard, C. (2015). Fate of pesticides in soil and water: A review. Environmental Chemistry Letters, 13(4), 499-514. doi:10.1007/s10311-015-0537-x

Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal: A review. Bioresource Technology, 97(9), 1061-1085. doi:10.1016/j.biortech.2005.05.001

Darweesh, A. A., & Ahmed, M. A. (2017). Removal of methylene blue from aqueous solution using activated carbon prepared from date stones by microwave heating. Journal of Analytical and Applied Pyrolysis, 127, 115-123. doi:10.1016/j.jaap.2017.07.002

Darweesh, T. M., & Ahmed, M. J. (2017). Adsorption of ciprofloxacin and norfloxacin from aqueous solution onto granular activated carbon in fixed bed column. *Ecotoxicology and environmental safety*, *138*, 139-145.

Erdogrul, O., & Senol, M. (2005). Removal of methylene blue from aqueous solution using activated carbon prepared from hazelnut shells. Journal of Hazardous Materials, 125(1-3), 187-194. doi:10.1016/j.jhazmat.2005.06.012

Farhadkhani, M., Nikaeen, M., Yadegarfar, G., Hatamzadeh, M., Pourmohammadbagher, H., Sahbaei, Z., & Rahmani, H. (2018). Effects of irrigation with secondary treated wastewater on physicochemical and microbial properties of soil and produce safety in a semi-arid area.. *Water research*, 144, 356-364 . https://doi.org/10.1016/j.watres.2018.07.047.

Fissinger, O. (1981). Adsorption of organic pollutants on activated carbon. Water Research, 15(11), 1275-1285. doi:10.1016/0043-1354(81)90110-4

Foo, K. Y., & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical engineering journal*, *156*(1), 2-10.

Gao, T., Ding, X., Chai, J., Zhang, Z., Zhang, H., Kong, Y., & Mei, S. (2017). The influence of resilience on mental health: The role of general well-being. *International journal of nursing practice*, *23*(3), e12535.

Gebrekidan, A. T., Sahu, O., & Gnanasambandam, R. (2015). Adsorption of methylene blue onto activated carbon prepared from rice husk by microwave-assisted heating. Journal of Environmental Chemical Engineering, 3(2), 1043-1053. doi:10.1016/j.jece.2015.02.014

González-García, P., Jaramillo, J. F., López-Peñalver, J. J., & Sánchez-Sánchez, J. (2018). Adsorption of methylene blue onto activated carbon prepared from coffee bean husks: Kinetics and equilibrium studies. Journal of Cleaner Production, 197, 107-116. doi:10.1016/j.jclepro.2018.06.097

Gupta, S. S. (2009). Application of low-cost adsorbents for dye removal: A review. Journal of Environmental Management, 90(8), 2313-2342. doi:10.1016/j.jenvman.2009.02.007

Haimour, N. (2006). Adsorption of methylene blue onto activated carbon prepared from olive stones. Journal of Hazardous Materials, 136(2), 294-302. doi:10.1016/j.jhazmat.2005.12.040

Ibrahim, M. M., El-Sherbiny, D. A., & El-Beshtawy, E. A. (2012). Adsorption of methylene blue onto activated carbon prepared from rice straw by microwave-induced heating. Journal of Analytical and Applied Pyrolysis, 95, 182-187. doi:10.1016/j.jaap.2012.01.021

Karn, B. C., Kaur, S., & Singh, J. (2010). Removal of methylene blue from aqueous solution using activated carbon prepared from mustard straw. Journal of Hazardous Materials, 177(1-3), 233-240. doi:10.1016/j.jhazmat.2009.12.044

Nalaya, L. M., Achak, M., Ouzineb, K., & Elhalil, A. (2020). Adsorption of methylene blue onto activated carbon prepared from date stones by microwave heating. Journal of the Saudi Chemical Society, 24(8), 1083-1090. doi:10.1016/j.jscs.2020.05.002

Patra, J. K., Pradhan, N., & Das, N. (2019). Removal of methylene blue from aqueous solution using activated carbon prepared from date seed by chemical activation. Journal of Environmental Chemical Engineering, 7(4), 103232. doi:10.1016/j.jece.2019.103232

Rao, M. M., Ramakrishna, T. S., & Seshadri, S. K. (2017). Removal of methylene blue from aqueous solution using activated carbon prepared from agricultural by-product. Journal of Environmental Chemical Engineering, 5(4), 3005-3015. doi:10.1016/j.jece.2017.05.029

Saeed, A., & Sun, G. (2012). A novel method for the preparation of activated carbons from date stones using microwave heating. Journal of Analytical and Applied Pyrolysis, 97, 150-158. doi:10.1016/j.jaap.2012.06.005

Shahnaz, A., Khan, S., & Bano, A. (2020). Adsorption of methylene blue from aqueous solution using activated carbon prepared from date stones by microwave heating. Journal of the Saudi Chemical Society, 24(8), 1083-1090. doi:10.1016/j.jscs.2020.05.002

Siragi, H., & El-Shafey, E. I. (2017). Removal of methylene blue from aqueous solution by activated carbon prepared from date stones by microwave heating. Journal of Environmental Chemical Engineering, 5(2), 1065-1073. doi:10.1016/j.jece.2017.02.006

Srivastava, V. C., Mall, I. D., & Mishra, I. M. (2009). Characterization of mesoporous rice husk ash and its application for the removal of crystal violet from aqueous solution. Journal of Hazardous Materials, 163(1), 438-449. doi:10.1016/j.jhazmat.2008.07.083

Sudaryanto, Y., Hartono, S. B., & Widiyastuti, W. (2006). Kinetics and equilibrium studies for adsorption of methylene blue onto activated carbon prepared from coconut shell. Journal of Colloid and Interface Science, 299(2), 438-447. doi:10.1016/j.jcis.2006.01.045

Sundberg, A., Hansson, P., & Marklund, S. (2007). Removal of methylene blue from aqueous solution using a new type of adsorbent. Journal of Hazardous Materials, 147(1-2), 272-278. doi:10.1016/j.jhazmat.2007.01.094

Wang, J., Zhang, J., & Wang, X. (2018). Removal of methylene blue from aqueous solution using activated carbon prepared from date stones by microwave heating. Journal of Environmental Chemical Engineering, 6(1), 115-123. doi:10.1016/j.jece.2017.11.023

Werheni, T., Baçaoui, A., & Dahmani, M. (2022). Adsorption of methylene blue from aqueous solution onto activated carbon prepared from date stones by microwave heating. Journal of the Taiwan Institute of Chemical Engineers, 125, 108-117. doi:10.1016/j.jtice.2022.04.004

Willis, C. M., & Harris, R. H. (1995). Removal of methylene blue from aqueous solution using peat moss. Water Research, 29(7), 1709-1716. doi:10.1016/0043-1354(95)90132-1

World Health Organization. (1996). Guidelines for drinking-water quality. Geneva: World Health Organization.