JEE Journal of Ecological Engineering

Journal of Ecological Engineering 2023, 24(12), 377–387 https://doi.org/10.12911/22998993/173490 ISSN 2299–8993, License CC-BY 4.0 Received: 2023.09.05 Accepted: 2023.10.20 Published: 2023.11.04

Water De-Chlorination by Non-Modified and Modified Biochar Derived from Date Palm

Sundus Khaleel Alfaiz¹, Dina Ali Yaseen^{2*}, Wisam A. Alawadi²

- ¹ Department of Material Engineering, College of Engineering, Univesity of Basrah, P.O. Box 49, Basrah, Iraq
- ² Department of Civil Engineering, College of Engineering, Univesity of Basrah, P.O. Box 49, Basrah, Iraq
- * Corresponding author's e-mail: dina.yaseen@uobasrah.edu.iq

ABSTRACT

The present study investigates the reduction of free residual chlorine (FC) from aqueous solution using nonmodified biochar (NM-B) and chemically modified biochar (M-B) derived from date palms. The role of biochar dose, biochar particle size, reaction time, solution pH, and initial concentration of FC on adsorption efficiency were assessed. The optimum contact time for higher FC uptake was reached after 20 min using NM-B and 8 min using M-B, with a biochar dose of 10 g/L. The optimum pH values and biochar size for higher FC adsorption were 4 and 0.6 mm, respectively. Higher removal was reached at 88% using NM-B and 96% using M-B. The pseudo-second-order model matched well with the kinetic outcomes. Langmuir isotherm was fitted well with the equilibrium results of FC uptake on NM-B and M-B, with regression coefficient (R²) values of 0.98 and 0.998, in that order. The separation parameter was within the limits of favorable adsorption of FC by both biochars. The higher uptake capacity (0.215 mg/g) was linked with the M-B, indicating that chemical modification of biochar was successful in increasing FC uptake from aqueous solutions. This study confirmed that utilizing biochar derived from date palms for FC removal is a very beneficial and cost-effective solution, especially in the countries that are considered the largest date producer in the world.

Keywords: adsorption, biochar, chemical modification, date palm, free chlorine

INTRODUCTION

Chlorine is an oxidizing chemical that mainly used during the disinfection process of drinking water in purification units. This attributed to the chlorine low cost and powerful effects comparing with other disinfections. After the addition of any chlorine form to the water during the chlorination process, chlorine is dissolved to hydrochloric acid (HCl), and hypochlorous acid (HOCl) that is hydrolyzed to hypochlorite (OCl) and hydrogen (H) ions. Both hypochlorite ions and hypochlorous acid are termed free residual chlorine (FC). The three forms of free chlorine are presented below Equations (1) and (2) (Kamel & Ismael, 2004):

 $Cl_{2} + H_{2}O = HOCl + H^{+} + Cl^{-}Eq.$ (1)

$$HOCl = H^+ + OCl^- Eq.$$
 (2)

The presence of FC is necessary during water transferring in the pipes for keeping the disinfection process continuous, as the water may be contaminated again after leaving the treatment plant. However, at point of use, the removal of FC to the recommended concentration is essential (Sheikhi et al., 2014). This because drinking water containing FC at a level of higher than 0.5 mg/L leads to inadmissible taste and scent, and consequently a humanity concern. Also, water linked with high concentration of FC could increase the risk of cancer or cause kidney, heart, lung, and liver illness. Additionally, excess FC damage the polyamide layer during the reverse osmosis stage in desalination units. Thus, the reduction of FC after disinfection is necessary and considered an important research area, especially in case of applying active and cost-effective technologies (Ogata et al., 2013). Water de-chlorination has been accomplished via applying various technologies like electrolysis, reverse osmosis, ion exchange, and adsorption. However, the recent attention highlights the applying of efficient and cost-effective technologies for treating chlorinecontaining water.

Recently, adsorption technology is considered the main focus of many researchers due to its low cost, easiness of usage, less chemical utilization, and superior effectiveness (Mustapha et al., 2019). Literature showed that several adsorbent materials have been used for free chlorine adsorption, like kaolinite clay (Kamel & Ismael, 2004), activated carbon derived from waste tires (Yousif, Yaseen, & Abu-Alhail, 2021), coal and coconut shell (Ogata et al., 2013) and bamboo charcoals (Asada et al., 2009).

Nowadays, biochar has been widely preferable for the adsorption of diverse water and wastewater pollutants. This attributed to the biochar features as an efficient and cheap material that utilizes simply and generates less by product wastes comparing with conventional choices. (Komnitsas & Zaharaki, 2016). As well as, biochar is considered a carbon rich material that has more absorbent sites and several functional groups (Aylan et al., 2023). Numerous biochar sources have been used successfully for pollutants adsorption, such as agricultural waste, shells, straws and woodchips. However, biochar derived from agricultural waste resources, such as grape seeds, grains, carob core, olive nucleus, walnut shells, and palm frond are well known as a cheapest option, especially in low income countries (Sklivaniotis et al., 2023). To achieve more uptake capacity, amendment techniques for biochar by magnetic, impregnation, physical, or chemical modifications is advisable. Modification process alerts the biochar properties by enhancing the surface area and porous structure of biochar, which is consequently increase the contaminants adsorption (Chemerys & Baltrenaite-Gediene, 2016; Dietrich et al., 2020; S. Wang et al., 2015).

In this context, there are limited applications that utilized biochar derived from palm frond for pollutants elimination. In addition, biochar derived from date palm for free residual chlorine adsorption has not been studied yet. Moreover, there is no available studies examined the role of chemically modified biochar for FC adsorption. Therefore, this study provides a valuable data regarding the role of using local and low cost biochar for free residual chlorine reduction. The current paper purpose is to examine the adsorption efficiency of free residual chlorine from aqueous solution using non-amended and chemically amended biochar's derived from date palm, based on kinetic and equilibrium tests. The impact of reaction time, mass and particle size of adsorbent materials, solution pH, and starting concentration on the FC reduction efficiency was also studied.

MATERIALS AND METHODOLOGY

The biochar used in this research was collected and produces from the date palm fronds (Phoenix dactylifera L.) in Abu Al-Khaseeb region (Basra City, Iraq). The source of the chlorine used in this study was Calcium hypochlorite Ca(OCl)₂, CAS number; 7778-54-3), which is supplied from Nirou Chlor Co. (Iran). The FC stock solution of 50 mg/L was able by melting an exact weight of Ca(OCl), in distilled water of 1 liter, and placed in darkness at temperature of 4 °C. The required concentration of FC (1-20 mg/L) was prepared by additional dilution. The solutions of sodium hydroxide (NaOH) and hydrochloric acid (HCl) supplied from local shop in Basrah. The reagents and chemicals uti lized in this work were analytical grade

The prepared (non- modified) biochar (PB) was made according to (Salem et al., 2021). The fronds of the date palms (*Phoenix dactylifera* L.) washed with tap water and dried under the sun heat for 15 days. Then, the dried fronds were chopped and placed in the furnace for around two hours (500–600 °C). After that, the biochar cooled, ground, and sieved based on the desired sizes (4.75, 2.36, 1.18, and 0.6 mm).

The modified biochar (MB) was prepared based on (Dietrich et al., 2020), by mixing the NM-B (5 g) with 0.1 M C₂H₆O, with ratio of 1:9. A magnetic stirrer at speed of 30 rpm was used to agitate the solution for 1 day at room temperature. Then, the resulted biochar was dried at temperature of 80°C until getting a stable weight. The non-modified (NM-B) and modified (M-B) were used for the adsorption of FC.

STUDY DESIGN

Batch experiments of FC adsorption

The batch works were operated for assessing the uptake capacity of FC on biochar surface based on different contact time, adsorbent load, adsorbent particle size, solution pH, and initial FC concentration. All experiments were operated triplicate.

The experiments of optimum contact time and adsorbent load were operated by mixing 0.1 g, 0.5 g, and 1 g of NM-B and M-B, individually, with 100 ml of FC solution. The initial FC concentration was 2.75 mg/L. This concentration was chosen as higher than the permissible limits that set by Water and Health Organization (Sarbatly & Krishnaiah, 2007), between 0.2 and 0.3 mg/L. The solution pH was kept without adjustment (8.49 ± 0.01) , and the adsorbents (biochar) particle size was 1.18 mm. Each solution was shaken using magnetic stirrer (at 150 rpm) at heating degree of 30 °C in 300 ml beaker. Each specific interval (1 to 35 min), sample 10 ml was taken, filtered by Whatman filters (0.45 µm), and tested to compute the remaining FC.

The study of optimum adsorbents size (4.75 and 0.6 mm) was conducted using the optimum dose of biochar at initial concentration of 2.75 mg/L. The solution pH was kept without amendment. The study of optimum solution pH 4-9 was conducted using the optimum dose and size of biochar at initial concentration of 2.75 mg/L. Both 0.1 M HCl and 0.1 M NaOH were used to adjust the solution pH, which is tested by HQ40d Portable Multi-Parameter Meter (www. hach.com). The impact of initial FC concentration study 0.5-20 mg/L was conducted based on the optimum pH, biochar size and dose. Each solution was shaken 150 rpm at heating degree of 30 °C in 300 ml beaker. After equilibrium time has achieved, samples were withdrawn, filtered, and tested for the determination of the remaining FC concentration. The removal (%) and adsorbed amount (mg/g biochar) of FC were determined by equations 3 and 4, respectively. The concentrations of FC tested by HANNA instrument (catalog number HI 93711), Free and Total Chlorine Photometer.

FC reduction % =
$$\left(\frac{C_1 - C_2}{C_1}\right) \cdot 100$$
 (3)

$$Q_e = \left(\frac{C_1 - C_e}{m}\right) \cdot vol \tag{4}$$

where: C_1 and C_2 – the starting and final FC concentrations (mg/L); C_e – the final concentration at equilibrium time (mg/L); vol – the volume of FC solution (ml); m – the biochar weight (g); Q_e – the uptake of FC at equilibrium time.

Kinetic study

The kinetic study was applied using 100 of FC solution mixed with 1 g of biochar (NM-B and M-B, separately). The FC solution at normal pH of 8.49 (non-neutralize) and concentration of 2.75 mg/L was shake for specific contact time, as mentioned before. The kinetics results were used to apply the pseudo-first order, pseudo-second order, and the intra-particle diffusion model, as described by the linear Equations 5, 6, and 7, respectively.

$$log(Q_e - Q_t) = \log Q_e - 0.434 \, b_1 \, t \qquad (5)$$

$$\frac{t}{Q_t} = \frac{1}{b_2 Q_e^2} + \frac{1}{Q_e} t$$
(6)

$$Q_t = b_3 \cdot t^{1/2} + C \tag{7}$$

where: Q_i – the amount of adsorbed material at time t (mg/g); b_1 , b_2 , and b_3 – the kinetic constants of pseudo first-order (min⁻¹), pseudo second order (g/mg·min), intra-particle diffusion (g/mg·min^{0.5}), respectively; t – the time (min); C – the constant linked with the boundary layer thickness (mg/g).

Isotherm study

Different isotherm models were used for determination the adsorption parameters and explain the adsorption processes. These isotherms are Langmuir (Equation 8). Freundlich (Equations 9), and Temkin (Equations 10). Equation 11 was used to determine the dimensionless equilibrium factor (EP), which used in Langmuir model to specify the nature of adsorption process.

$$\frac{1}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{b_4 Q_{max} C_e} \tag{8}$$

$$loqQ_e = \log D + \frac{1}{n} logC_e \tag{9}$$

$$Q_e = K_1 \ln K_2 + K_1 \ln C_e$$
 (10)

$$EP = \frac{1}{1 + C_1 \cdot b_4} \tag{11}$$

where: Q_{max} – the maximum quantity of the FC adsorbed per mass of biochar (mg/g); b_4 – the Langmuir constant linked with the adsorption energy (L/mg); D – the Freundlich constant of uptake (mg/g); n – the dimensionless parameter of adsorption intensity; k_1 – the constant depends on the adsorption temperature (L/g); k_2 – the dimensionless constant of Temkin isotherm; EP – the equilibrium parameter.

RESULTS AND DISCUSSION

Characteristics of biochar derived from date palm

In general, biochar has high BET surface area and carbon content, and rich with aromatic and aliphatic structure, and therefore being a perfect adsorbent material (Davidson, 2023; Tahir, Al-Obaidy, & Mohammed, 2020). Date palm is a common tree that widespread in Gulf region. The moisture and ash contents of date palm biomass were approximately 8.4% and 5.2%, respectively. After date palm pyrolysis at temperature between 500 and 600 °C for biochar production, the moisture content was ranged from 2.55% to 2.01%, and ash content was ranged from 18.44% and 19.9%. Modification process increases the moisture and ash contents to 3.42% and 44.6%, respectively. Both moisture and ash contents of biochar were measured based on (Inegbedion & Ikpoza, 2022)

Parameters affecting FC adsorption on biochars

Impact of Biochar mass and contact time

Quantity of biochar and contact time for optimum FC adsorption has crucial role during the adsorption process. Outcomes displayed that the removal rates of FC using NM-B were increased with the time for all masses, especially during the first five minutes (Fig. 1). After equilibrium time has reached, the FC reduction was lower (48%) using the smaller adsorbent concentration (1 g/L). However, the removal was increased to 56% and 61% using 5 g/L and 10 g/L of NM-B, in that order. Similarly, the reduction rate of FC using M-B was increased with time. Also, the removal rate after the equilibrium time was higher 67% and 72% using 5 g/L and 10 g/L, in that order, and lower (59%) using 1 g/L of M-B (Fig. 2). The lower adsorption rate by the lower adsorbent dosage in case of using NM-B or M-B interpreted by the presence of less surface area, and therefore less adsorption sites due to the low amount of biochar (Ambaye et al., 2021; Komnitsas & Zaharaki, 2016; X. Wang et al., 2006). All the removal values of FC using the three dosages of adsorbents were higher using M-B compared with the corresponding values using NM-B. This because the chemical modification increased the biochar porosity and surface area, improving the biochar chemical functional group, as well as increasing the sorption sites that boosted

the chemical binding with pollutants (S. Wang et al., 2015; X. Wang et al., 2020).

Overall, M-B was improved the removal of FC. In addition, 10 g/L was the optimum dosage for higher FC adsorption by both adsorbents, which was selected for the further experiments. The contact time study showed that the reduction rate of FC by NM-B and M-B was increased noticeably with increasing the interaction time. This was due to the occurrence of adsorption process by the active sites on the adsorbents, as these sites enable the FC to bind onto the biochar surface (Jaguaribe et al., 2005). The interaction time highly affect the adsorbate transmission onto the positions of biochar. Regarding the NM-B, the removal increment has stopped after 6 min when applying NM-B dosage of 1 g/L, and 20 min in case of applying NM-B dose of 5 g/L and 10 g/L, which indicates that the equilibrium time has achieved (Fig. 1). However, the removal increment has stopped after 4 min when applying M-B dosage of 1 g/L, and 8 min in case of applying M-B dosage of 5 g/L and 10 g/L (Fig. 2). At equilibrium time, the removal rate reach to a stable magnitude because the adsorption rate of FC onto biochar was same as the desorption rate (Sahu et al., 2021).

So, the optimum contact time achieving maximum rate of FC adsorption using 10 g/L of NM-B (61%) and MB (72%) was 20 min and 8 min, respectively. The optimum time was considered for the further studies. The adsorption value of FC of more than 60% using both modified and non-modified biochar may belong to the pyrolysis temperature chosen in this study, which was 500-600° C. This because the sorption efficiency of pollutants increased using biochar prepared under fast pyrolysis (500–700 °C) conditions (Murtaza et al., 2022; Shen et al., 2017), which alert the chemical bonds arrangement in the raw material and create new functional groups.

Impact of particle size

The particle size study of NM-B and M-B for optimum FC reduction was examined depending on the results of optimum biochar dose and contact time. Therefore, residence time of 20 min and 8 min were applied during the examination of different sizes of NM-B and M-B, respectively. A biochar dose of 10 g/L was mixed with 100 ml of FC solution at concentration of 2.75 mg/L using magnetic stirrer at 150 rpm till the equilibrium time has reached. The solution heating degree



Figure 1. Rate of free residual chlorine reduction (FC) at different doses and time by (a) non-modified biochar (NM-B), (b) modified biochar (M-B) (concentration – 2.75 mg/L, particle size – 1.18 mm, pH – 6.5-7, speed – 150 rpm).

was kept 30 °C, the pH value of FC solution was not adjusted. The selected diameters of biochar particles were 4.75, 2.36, 1.18, 0.6, and 0.2 mm. The outcomes presented those lower particles sizes of both biochar were linked with higher FC adsorption (Fig. 2). Same results confirmed (Ali & Gupta, 2006), authors mentioned that the small grain size may be minimized the stagnant film depth that surrounding the particle, and as a result the distances inside the voids reduced. Also, small particle sizes provide extra surface area for pollutant adsorption (Yousif et al., 2021). The highest FC removal values were not significant in case of using 0.6 mm or 0.2 mm of biochar particles, for both NM-B and M-B. Therefore, a size of 0.6 mm was chosen for further study as the optimum size of biochar particles.

Impact of pH

In general, biochar surface has a negative charge and a high pH value, which resulting much adsorption for cations, and weak adsorption for anions (X. Wang et al., 2020). Therefore, at natural conditions the adsorption rate of FC may be due to the endothermic reaction mechanism or belong to the impact of fast pyrolysis of more than 500 °C during biochar preparation, which helps to enhance the removal of pollutants, compared with the slow pyrolysis of less than 400 °C (Shen et al., 2017). However, pH modification is also required to increase the removal of FC. In this study the solution pH without adjustment was 8.49. The pH study was conducted using different pH solutions of 4, 5, 6, 7, 8 and 9, to cover the acidic, neutral, and basic conditions. The other parameters were remained same (biochar dose of 10 g/L was mixed with 100 ml of FC solution at concentration of 2.75 mg/L using magnetic stirrer at 150 rpm till the equilibrium time has reached, the solution temperature was maintained at 30°C, and particles size of 0.6 mm).

Results showed that the removal was increased from 56% to 78% by NM-B (Fig. 3a), and





from 64% to 87% by M-B (Fig. 3b). The noticeable improvement of biochar adsorption capacity at low pH values was because the negatively charged chlorine was attracted by the positively charged biochar surface due to H⁺ ions enhancement in the acidic solution (Sahu et al., 2021). This because the adsorption process by biochar is affected by the oxygen-containing functional groups that is linked with the solution pH (Ambaye et al., 2021).

Impact of initial FC concentration

The impact of starting FC concentration was assessed using FC concentrations ranging between 0.5 and 20 mg/L. The other parameters were kept as determined by earlier experiments. The biochar dose of 10 g/L at size of 0.6 mm was mixed with 100 ml of FC using magnetic stirrer at 150 rpm till the equilibrium time has reached. The solution temperature and pH were kept 30° C and 4, in that order. The outcomes declared that the reduction of FC was decreases with increasing the starting concentration using modified or non-modified biochar (Fig. 4). This because when active sites on the biochar surface reached to the saturation point, and consequently the available sites number was not enough to adsorb more chlorine at higher concentrations (Sahu et al., 2021; Suneetha et al., 2015).

Adsorption kinetic of free residual chlorine

Free chlorine adsorption on both non-modified and modified is shown in Figure 5. The higher uptake of 0.132 mg/g NM-B and 0.166 mg/g M-B was reached after 20 min and 8 min, respectively. Modified biochar was the best FC adsorption performance.

The kinetic results were fitted with mathematical equations related to different kinetic models, for understanding the FC adsorption mechanisms





Figure 3. Rate of free residual chlorine (FC) reduction using different values of pH (concentration; 2.75 mg/L, dose; 10g/L, speed; 150 rpm; particle size, 0.6 mm). (a) non-modified biochar at time 20 min (NM-B), (b) modified biochar (M-B) at time 8 min







Figure 5. Uptake capacity of free chlorine on both non-modified (NM-B) and modified (M-B) biochar

and the pathway of the occurred reactions during the process of transferring FC from liquid phase to the solid phase. Table 1 presents the kinetic of FC adsorption and the parameters calculated from the three models. The schemes of pseudo first-order model for the time against log $(Q_a - Q_t)$ using NM-B and M-B are shown in Figs. 6a and b, in that order. The magnitudes of b₁ and predicted Q are calculated based on the slope and intercept of the plot, in that order. The plot of pseudo second-order model for the time versus t/Q_t using NM-B and M-B are presented in Figs.6 c and d, respectively. The values of b, and predicted Q are calculated based on the slope and intercept of the plot, in that order. The plots of Intra-particle diffusion model between t^{0.5} versus Q_t using NM-B and M-B are shown in Figs 6e and f. The values of b₃ was calculated based on the slope of the plot.

The low values of b_1 and b_3 linked with pseudo-first order model and intra-particle model indicated the occurrence of slow adsorption processes using both NM-B and M-B. However, the values of b_2 resulted by pseudo-second order model was higher using both NM-B and M-B, confirming the occurrence of high rate of adsorption. Also, the correlation coefficient value (R^2) was higher by applying pseudo-second-order model compared with other models. Furthermore, the value of experimental Q_t was more in accordance with the Q_t calculated from the equation of pseudo-second order model. Therefore, the adsorption data of FC adsorption is more fitted with pseudo-second-order model (Figure 6). This confirmed the occurrence of chemical adsorption process. Also, the valence forces between biochar and FC could be part of the adsorption (Ünlü & Ersoz, 2007).

Adsorption isotherm modeling

Three common equations were used to understand the adsorption isotherm of FC on biochar, and each model depends on specific assumptions. The Langmuir model assumed that the maximum adsorption capacity depends on the saturated monolayer of FC molecules on the homogeneous biochar surface. The Freundlich model assumed the occurrence of multilayer adsorption process on a heterogeneous surface of the adsorbent. The

Table 1. Kinetic parameters of the three models for the adsorption of FC on to biochar

Kinatia madala	Baramatara		MP
Kineuc models	Farailleters	INIVI-D	IVI-D
Pseudo-first-order	Q _e (exp.)	0.132	0.166
	Q _e (cal.)	0.087	0.169
	b ₁	2.540	0.539
	R ²	0.852	0.976
Pseudo second-order	Q _e (cal.)	0.133	0.168
	b ₂	29.573	28.761
	R ²	0.999	1.000
Intra-particle diffusion	b ₃	0.014	0.017
	С	0.074	0.097
	R ²	0.425	0.405

Note: NM-B; non-modified biochar, M-B; modified biochar.



Figure 6. Plots of pseudo first-order kinetics (a and b), pseudo second-order kinetics (c and d), and intra-particle diffusion model (e and f) for FC adsorption on non-modified (a, c, and e), and modified (b, d, and f) biochar

Tompkins model assumed that the binding energies are distributed homogeneously, as well as all FC molecules on the adsorbent surface shows a linear decline in terms of the adsorption heat (Yousif et al., 2021).

Table 2 presents the correlation coefficients (R^2) values and the determined constants related

to the three studied models. The values of Q_{max} and b_4 were calculated from the slope and intercept of C_e against C_e/Q_e , respectively, based on Fig. 7a (NM-B) and Fig. 7b (M-B). Both n and D values were determined from the slope and intercept of log C_e against log Q_e , respectively, based on Fig. 7c (NM-B) and Fig. 7d (M-B). Both K_1 and

 Table 2. Constants of the adsorption isotherms for FC adsorption on non-modified and modified biochar (Note: NM-B; non-modified biochar, M-B; modified biochar)

Isotherm	Parameters	NM-B	M-B
Langmuir	Q _{max}	0.208	0.215
	b ₄	1.838	4.853
	R ₂	0.980	0.998
	EP	0.165	0.069
Freundlich	n	3.504	6.570
	D	0.135	0.176
	R ₂	0.787	0.832
Temkin	K ₁	0.043	0.028
	K ₂	23.216	598.800
	R ₂	0.810	0.846



Figure 7. Plots of Langmuir (a and b), Freundlich (c and d), and Temkin (e and f) isotherms for FC adsorption on non-modified (a, c, and e), and modified (b, d, and f) biochar

 K_2 values were calculated based on the slope and intercept of ln C_e against Q_e, respectively, based on Fig. 7e (NM-B) and Fig. 7f (M-B). Results showed that R² linked with Langmuir model for both NM-B and M-B was higher than other models. These results confirmed that Langmuir equation is best fitted with the experimental outcomes as the predominated model for demonstrating FC adsorption on the biochar surface.

The higher Q_{max} was linked with the adsorption process by M-B, indicating that chemical modification of biochar was successful to enhance the reduction of FC. The values of equilibrium factor (EP) for both NM-B and M-B were between zero and 1 (Table 2), demonstrating that the adsorption of FC is favorable at the study conditions (Fierro, Torné-Fernández, Montané, & Celzard, 2008; Hameed, Tan, & Ahmad, 2008; Tie et al., 2017). The data indicated that the lowest EP magnitude was belong to M-B confirming its favorable behavior for the adsorption of FC.

Note that, the high adsorption capacity of FC by biochar derived from date palms is very beneficial and cost effective because Iraq is one of the largest date producers in the world.

CONCLUSIONS

The adsorption study using biochar derived from date palm concluded that the FC adsorption onto both non-modified and modified biochar was successfully achieved. The optimum contact time for higher FC uptake was reached after 20 min using NM-B and 8 min using M-B, with a biochar dose of 10 g/L. The optimum pH values and biochar size for higher FC adsorption was 4 and 0.6 mm, respectively. Higher removal was reached to 88% using NM-B and 96% using M-B. Pseudosecond order model fits best with the kinetic data, and Langmuir adsorption isotherm was fitted well with the experimental data of FC adsorption on NM-B and M-B with the regression coefficient (R^2) of 0.98 and 0.998, respectively. The adsorption behavior was within the limits of favorable adsorption by both NM-B and M-B. The higher uptake capacity was linked with the M-B, indicating that chemical modification of biochar was beneficial to enhance the removal of FC from aqueous solutions.

This study suggests that date palm biochar is a feasible approach that offers an economical solution for water de-chlorination and agricultural waste management. This approach is widely recommended in countries that commonly known as a date producer.

Acknowledgment

Authors thank the researcher Rana A. Aylan for her technical support.

REFERENCES

- Ali, I., & Gupta, V. (2006). Advances in water treatment by adsorption technology. Nature protocols, 1(6), 2661-2667.
- 2. Ambaye, T., Vaccari, M., van Hullebusch, E.D., Amrane, A., & Rtimi, S. (2021). Mechanisms and adsorption capacities of biochar for the removal of organic and inorganic pollutants from industrial wastewater. International Journal of Environmental Science and Technology, 1-22.
- Asada, T., Okazaki, A., Kawata, K., & Oikawa, K. (2009). Influence of pore properties and solution pH on removal of free chlorine and combined chlorine by porous carbon. Journal of Health Science, 55(4), 649-656.
- Aylan, R.A., Al-Abbawy, D.A., & Yaseen, D.A. (2023). Development of the Horizontal Flow Wetland Using Palm Waste Biochar for Greywater Reclamation. Journal of Ecological Engineering, 24(8).
- Chemerys, V., & Baltrenaite-Gediene, E. (2016). Modified biochar: a review on modifications of biochar towards its enhanced adsorptive properties.
- Davidson, M.K. (2023). Biochar from date palm (Phoenix dactylifera L.) residues—a critical review. Arabian Journal of Geosciences, 16(2).
- Dietrich, C.C., Rahaman, M.A., Robles-Aguilar, A. A., Latif, S., Intani, K., Müller, J., & Jablonowski, N.D. (2020). Nutrient loaded biochar doubled biomass production in juvenile maize plants (*Zea mays* L.). Agronomy, 10(4), 567.
- Fierro, V., Torné-Fernández, V., Montané, D., & Celzard, A. (2008). Adsorption of phenol onto activated carbons having different textural and surface properties. Microporous and mesoporous materials, 111(1-3), 276-284.
- Hameed, B., Tan, I., & Ahmad, A. (2008). Adsorption isotherm, kinetic modeling and mechanism of 2, 4, 6-trichlorophenol on coconut husk-based activated carbon. Chemical engineering journal, 144(2), 235-244.
- 10. Inegbedion, F., & Ikpoza, E. (2022). Estimation of the moisture content, volatile matter, ash content, fixed carbon and calorific values of rice husk

briquettes. Paper presented at the Proceedings of the International Conference on Industrial Engineering and Operations Management Nsukka, Nigeria.

- Jaguaribe, E.F., Medeiros, L.D.L., Barreto, M.D.C.S., & Araujo, L.P.D. (2005). The performance of activated carbons from sugarcane bagasse, babassu, and coconut shells in removing residual chlorine. Brazilian Journal of Chemical Engineering, 22, 41-47.
- Kamel, M.M., & Ismael, A.M. (2004). Abatement of free chlorine from water using Kaolinite clay. Ass. Univ. Bull. Environ. Res, 7(2), 117-124.
- Komnitsas, K.A., & Zaharaki, D. (2016). Morphology of modified biochar and its potential for phenol removal from aqueous solutions. Frontiers in Environmental Science, 4, 26.
- 14. Murtaza, G., Ahmed, Z., Dai, D.-Q., Iqbal, R., Bawazeer, S., Usman, M., et al. (2022). A review of mechanism and adsorption capacities of biocharbased engineered composites for removing aquatic pollutants from contaminated water. Frontiers in Environmental Science, 10, 2155.
- Mustapha, S., Shuaib, D., Ndamitso, M., Etsuyankpa, M., Sumaila, A., Mohammed, U., & Nasirudeen, M. (2019). Adsorption isotherm, kinetic and thermodynamic studies for the removal of Pb (II), Cd (II), Zn (II) and Cu (II) ions from aqueous solutions using Albizia lebbeck pods. Applied water science, 9, 1-11.
- 16. Ogata, F., Tominaga, H., Ueda, A., Tanaka, Y., Iwata, Y., & Kawasaki, N. (2013). Application of activated carbons from coal and coconut shell for removing free residual chlorine. Journal of oleo science, 62(4), 241-244.
- 17. Sahu, N., Bhan, C., & Singh, J. (2021). Removal of fluoride from an aqueous solution by batch and column process using activated carbon derived from iron infused Pisum sativum peel: characterization, Isotherm, kinetics study. Environmental Engineering Research, 26(4).
- Salem, I.B., El Gamal, M., Sharma, M., Hameedi, S., & Howari, F.M. (2021). Utilization of the UAE date palm leaf biochar in carbon dioxide capture and sequestration processes. Journal of Environmental Management, 299, 113644.
- Sarbatly, R.H., & Krishnaiah, D. (2007). Free chlorine residual content within the drinking water distribution system. International Journal of Physical Sciences, 2(8), 196-201.
- 20. Sheikhi, R., Alimohammadi, M., Askari, M., & Moghaddasian, M.S. (2014). Decay of free residual chlorine in drinking water at the point of use. Iranian journal of public health, 43(4), 535.
- Shen, Z., Zhang, Y., McMillan, O., Jin, F., & Al-Tabbaa, A. (2017). Characteristics and mechanisms of nickel adsorption on biochars produced from wheat

straw pellets and rice husk. Environmental Science and Pollution Research, 24, 12809-12819.

- Sklivaniotis, L.N., Economou, P., Karapanagioti, H.K., & Manariotis, I.D. (2023). Chlorine removal from water by biochar derived from various food waste natural materials. Environmental Processes, 10(1), 4.
- 23. Suneetha, M., Sundar, B.S., & Ravindhranath, K. (2015). Removal of fluoride from polluted waters using active carbon derived from barks of Vitex negundo plant. Journal of Analytical Science and Technology, 6(1), 1-19.
- 24. Tahir, A.H., Al-Obaidy, A.H.M., & Mohammed, F.H. (2020). Biochar from date palm waste, production, characteristics and use in the treatment of pollutants: A Review. Paper presented at the IOP Conference Series: Materials Science and Engineering.
- 25. Tie, J., Fang, X., Wang, X., Zhang, Y., Gu, T., Deng, S., et al. (2017). Adsorptive Removal of a Reactive Azo Dye Using Polyaniline-Intercalated Bentonite. Polish Journal of Environmental Studies, 26(3).

- 26. Ünlü, N., & Ersoz, M. (2007). Removal of heavy metal ions by using dithiocarbamated-sporopollenin. Separation and Purification Technology, 52(3), 461-469.
- 27. Wang, S., Gao, B., Li, Y., Mosa, A., Zimmerman, A.R., Ma, L.Q., et al. (2015). Manganese oxidemodified biochars: preparation, characterization, and sorption of arsenate and lead. Bioresource technology, 181, 13-17.
- Wang, X., Guo, Z., Hu, Z., & Zhang, J. (2020). Recent advances in biochar application for water and wastewater treatment: a review. PeerJ, 8, e9164.
- Wang, X., Sato, T., & Xing, B. (2006). Competitive sorption of pyrene on wood chars. Environmental science & technology, 40(10), 3267-3272.
- 30. Yousif, Y.T., Yaseen, D.A., & Abu-Alhail, S. (2021). A Comparative Study for Attenuation of Residual Free Chlorine by Mesoporous Adsorbent from Scrap Tire Rubber and Commercial Activated Carbon. Journal of Green Engineering, 11, 2170-2187.