



Low-cost corn cob biochar for pesticides removal from water

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Abstract

This work aimed to study the isotherm and kinetics of adsorption of a mixture of 10 pesticides (viz., atrazine, chlorfenvinphos, chlorpyrifos, cyprodinil, diazinon, dimethoate, diuron, ethion, malathion, and profenofos) on corn cob biochar (CCB) in an aqueous solution. CCB is a low-cost adsorbent produced from pyrolysis at 500°C for 3 h in an oxygen-limited condition. It was characterized by Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier-transform infrared (FTIR) spectroscopy. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) was used to determine the residual pesticide concentration. Adsorption equilibrium and kinetics were investigated by using batch adsorption experiments. The optimized pH, contact time, adsorbent dose, and initial pesticides concentration for the maximum adsorption rates were found to be 3, 60 min, 10 g/L, and 500 µg/L, respectively. The sorption of all pesticides by CCB was found to enhance by decreasing pH; since the removal percentage of atrazine increased from 57 to 74 % by decreasing the pH from 9 to 3. The Langmuir model represented the adsorption process better than the Freundlich model with R² values ranging from 0.957 to 0.999. Adsorption kinetic data were fitted well with the pseudo-first order kinetic model. Accordingly, CCB can be used as an effective low-cost agricultural waste that could be applied for removing pesticide residues from water.

Keywords: Corn cob biochar; adsorption; pesticides; water pollution; LC-MS/MS.

1. Introduction

Water pollution by pesticides used in agriculture and public health sectors is currently a major concern worldwide, prompting the need for efficient remediation techniques. Over the past decade, pesticide usage to control pests surpassed 4 million tons annually worldwide [1]. Less than 1% of the applied pesticides can reach to the target pests [2,3]. Thus, the remaining percent of pesticides used end up in the environment, where they are contaminating the nearby water bodies through precipitation, surface runoff, and soil leaching, which will worsen the water quality [4]. The presence of multiple pesticide residues in the aquatic environment, can cause detrimental effects on aquatic organisms and eventually human beings [5].

Despite the availability of advanced treatment techniques such as photo-Fenton, advanced oxidation processes, photocatalytic oxidation/ degradation, membrane processes, electrochemical oxidation/ degradation, biological treatment, and combined methods[6–8] for the removal of pesticides, the adsorption process remains the best due to its low-cost, ease of operation, flexibility, insensitivity to toxic pesticides, and high efficiency [9].

Biochar is one of the most effective adsorbents and can be obtained through the pyrolysis of agri-wastes biomass under oxygen-limited conditions[10]. Every year, millions of tons of agricultural wastes are generated around the world as a result of varied crop production and processing, constituting a sustainable, renewable resource, and a potential low-cost

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feedstock for biochar production[11].

During the last decade, there has been a steady increase in the number of studies on the use of biochar as promising adsorbents for pesticide removal from water[12–15]. However, research on the optimal adsorption conditions, isotherm, and kinetics of a mixture of pesticides by corn cob biochar (CCB) in an aqueous solution is rarely investigated.

Therefore, this study aimed to study the isotherm and kinetics of adsorption of a mixture of ten pesticides in an aqueous solution by CCB which was characterized for its physico-chemical properties as well.

2. Materials and methods

2.1. Chemicals and reagents

All studied pesticides standards (viz., atrazine, chlorpyrifos, chlorfenvinphos, cyprodinil, diazinon, dimethoate, diuron, ethion, malathion and profenofos) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Methanol (HPLC grade) was purchased from Sigma Aldrich (USA). All the glassware were grade (A) from (Hirschmann Laboratory GmbH). Milli-Q water ($\geq 17.6 \Omega\text{-cm}$) was supplied by the Millipore water purification system (Milli-Q).

A stock standard solution of each pesticide was prepared in 100% methanol with a concentration of 1000 $\mu\text{g/mL}$. A mixture of these ten pesticides with individual pesticide concentrations of 40 $\mu\text{g/mL}$ was prepared in a 1:1 methanol: Milli-Q water solution. Calibration of pesticides mixture with concentration levels of 0.005, 0.01, 0.05, 0.1, and 0.5 $\mu\text{g/mL}$ were freshly prepared in Milli-Q water.

2.2. Adsorbents

Biochar was prepared from abundant and a low-cost corn cob (CC) agricultural waste. Prior to pyrolysis CC was dried at 100 °C for 24h and cut to small pieces ($\leq 3\text{cm}$). Then was pyrolyzed at 500 °C for 3h in a muffle furnace (F6000 Bench-Top Muffle Furnace, Thermo-Thermolyne) under limited oxygen. The resulted biochar was collected, ground using a mortar and pestle then passed through a 160 μm sieve and washed with Milli-Q water, then dried overnight at 110°C using a drying oven. The produced biochar was stored in air-tight PTFE containers at room temperature until usage.

2.3. Characterization of prepared biochar

Ash content of CCB was analyzed according to the standard AOAC Official Method 923.03[16]. Moisture content was determined by Halogen Moisture Analyzer (HR73-METTLER TOLEDO). The pH was measured by soaking CCB in Milli-Q water at a ratio of 1:50 for 2 h with shaking; the slurry pH was then measured with a Seven Compact pH meter S210.

Scanning electron microscopy analysis (SEM) images of CCB were used to determine the surface morphology of the prepared CCB using (SEM-Quanta FEG-250, ESEM, Netherlands). CCB was coated by Gold Sputter Coater (Model: Edwards S150B; Manufacturer: BOC Edwards, UK).

Fourier transform infrared (FTIR) spectroscopy (Bruker vertex80 v, Germany) was used to identify the surface functional groups of CCB in the range of 400-4000 cm^{-1} with resolution 4 cm^{-1} .

X-ray diffraction (XRD) was used to characterize the crystallinity and mineralogical composition of CCB by Empyrean X-ray diffractometer (PANalytical B.V., Netherlands), under the condition of the range 4° to 80° 2 θ , 45 kV voltage, 30 mA current, the goniometer scanning speed is 8°/min and step is 0.026°.

Brunauer–Emmett–Teller (BET) method was utilized to investigate the specific surface area and total pore volume of CCB [17] using a high-throughput surface area and pore size analyzer (NOVA touch LX4, USA) via liquid nitrogen adsorption at 77.3 K using an automatic adsorption gas system.

2.4. Adsorption experiments

The sorption of a mixture of ten pesticides on CCB was determined using a batch equilibrium method. Briefly, 0.25 g of CCB and 22.5 mL of Milli-Q water were placed in a 50-mL centrifuge tube. All the tubes were agitated on a reciprocal shaker at 120 rpm at the ambient temperature ($25 \pm 0.2^\circ\text{C}$) for 2 h to homogenize the CCB with water before adding the pesticide mixture. Then, 2.5 mL of a mixture of the ten pesticides was added to all tubes to reach the final concentration of each pesticide of 500 $\mu\text{g/L}$. Control samples were treated similarly without adding adsorbent. Samples were collected at different time intervals and centrifuged for 5 minutes at 4500 rpm. Eventually, a portion of the aqueous supernatant was collected and filtered through a 0.45 μm PTFE acrodisc syringe filters into a vial for direct analysis with LC-MS/MS.

The amount of pesticide (mg) per unit mass of adsorbent (g) at equilibrium (q_e) was calculated as shown in Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where q_e is the adsorption capacity of pesticides (mg/g), C_0 is the initial pesticide concentration in the liquid phase (mg/L), C_e is the pesticide concentration at equilibrium (mg/L), V is the volume of solution (L) and W is the mass of adsorbent used (g).

The removal percent of pesticides from the solution was determined as in Eq. (2):

$$\text{Removal (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

Where C_0 and C_e are the initial and equilibrium pesticides concentration.

Four main factors that affect the efficiency of pesticides adsorption were described as follow:

2.4.1. Effect of contact time

The adsorption of the pesticides mixture on CCB was tested at different time intervals (10, 20, 30, 40, 50, 60, 90, 120, 180, 240 minutes, and 24 hours) while maintaining the other parameters fixed (500 $\mu\text{g/L}$ pesticides concentration, 10 g/L mass of CCB, pH=8, at room temperature (25 ± 0.2 °C)).

2.4.2. Effect of CCB mass (g/L)

Five different mass adsorbents of CCB (2, 4, 10, 20, and 30 g/L) were studied at initial pH 8, at room temperature (25 ± 0.2 °C), pesticides concentration of 500 $\mu\text{g/L}$, and a contact time of 60 minutes.

2.4.3. Effect of pH

Three different pH levels (3, 5, and 7) were examined in addition to the initial pH solution 8 with constant mass adsorbent of 10 g/L, pesticides concentration of 500 $\mu\text{g/L}$ at room temperature (25 ± 0.2 °C), and a contact time of 60 minutes.

2.4.4. Effect of pesticides initial concentration

Three additional pesticides concentrations of 200, 800, and 1000 $\mu\text{g/L}$ were tested in addition to the previous pesticides' concentrations of 500 $\mu\text{g/L}$, at fixed mass adsorbent of 10 g/L, at room temperature (25 ± 0.2 °C) and a contact time of 60 minutes.

All previous experiments were performed in duplicates, and the mean values were calculated. The control samples without adsorbents were also studied

to exclude any potential effect on the pesticides (the control samples and all tubes were covered with aluminum foil to avoid possible photo-catalysis of any pesticide).

2.5. Adsorption isothermal models

The Langmuir and Freundlich isotherm models were applied to understand the interactions between pesticides and CCB.

2.5.1. Langmuir isothermal model

Langmuir isothermal model assumes that the adsorbent has a homogeneous surface with identical adsorption sites and only can be covered by a complete monolayer. The linear form of Langmuir isotherm [18] is shown in Eq. (3):

$$\frac{C_e}{C_{\text{ads}}} = 1/Q_b + C_e/Q \quad (3)$$

where C_e is the equilibrium concentration of pesticides in solution (mg/L), C_{ads} is the amount of pesticides sorbed per unit mass of CCB (mg/g), and Q and b are Langmuir constants related to sorption monolayer capacity (mg/g) and sorption energy (L/mg), respectively.

The dimensionless constant separation factor R_L value is calculated from the Langmuir isotherm constant b and pesticides initial concentrations (C_0) as presented below [19]:

$$R_L = \frac{1}{(1 + b C_0)} \quad (4)$$

R_L is that explains the shape and favorability of the adsorption between CCB and pesticides. The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

2.5.2. Freundlich isothermal model

The empirical Freundlich isotherm assumes that the adsorbent has a heterogeneous adsorbent surface with non-uniform adsorption sites and describes the reversible adsorption process. The linear form of Freundlich isotherm can be expressed as shown in Eq. (5) [20]:

$$\log C_{\text{ads}} = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

Where k_f represents the adsorption capacity (L/mg) for the adsorbent and $1/n$ is adsorption

intensity which is related to the heterogeneity of the adsorbent surface.

2.6. Kinetic models

To fit the experimental data, two kinetic models were used, the pseudo-first order (PFO) kinetic model (Eq. 6) and the pseudo-second order (PSO) kinetic model (Eq. 7)[21,22]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where: k_1 (h^{-1}) is the PFO rate constant and k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{h}^{-1}$) is the PSO rate constant are the adsorption rate constants, q_t and q_e are the pesticides sorption capacity at time t and at equilibrium, respectively (mg kg^{-1}).

2.7. LC-MS/MS analysis

The used LC-MS/MS technique was an API 6500+ tandem mass spectrometer (AB SCIEX). The used ionization mode was the soft electrospray ionization source (ESI). A Shimadzu HPLC system (Exion LC) with C18 solvent saver LC column from Agilent (proshell 120, 3 mm \times 50 mm \times 2.7 μm) was used. The mobile phase components consisted of solvent (A): a mixture of Milli-Q water: Methanol (9:1, v: v) of pH 4, using ammonium formate; and solvent (B): methanol. The runtime of 4 min was applied for the analysis of the ten tested pesticides in water. The mobile phase was pumped at a flow rate of 0.5 mL/min with solvent gradient program, as follows: 0–1.9 min the program is held constant at 80 % from B, 1.9–2 min linear gradient to 95 % from B; gradient to return to 80 % until end run time 4 min. The mass parameters were an ion spray voltage of 5500 V, ion source temperature of 450 °C, curtain gas pressure of 25 psi, an atomization air pressure of 45 psi, the auxiliary gas pressure of 45 psi, and an entrance potential of 10 V. Multiple Reaction Monitoring (MRM) separation and detection mechanism was used to support quantitation by confirmation ion using positive ionization.

2.8. Statistical analysis

All experiments were performed in duplicates. The parameters of adsorption isotherm, adsorption kinetic data, and the correlation coefficients (R^2) were

calculated by Microsoft excel 2016. The graphs were made using Minitab® 19.2 program.

3. Results and discussion

3.1. Characterization of biochar

3.1.1. pH and proximate analysis

pH measurements showed that corn cob biochar (CCB) was alkaline. Previous studies showed that most of the adsorbents biochar is alkaline, due to the presence of alkaline elements (Na, K, Ca, and Mg) as well as calcite major components of biochar ash[23]. Hence, the increase in ash content is mainly attributed to the increase in the amount of alkali metal during the pyrolysis; the increase in pH of the biochar mainly comes from these mineral salts[24–26], when biochar is dissolved, these alkaline substances are dissolved in water to increase the pH. The results in Table 1 indicate that CCB has a high pH=8 due to its high percentage of ash 43.5%, compared with a moisture content which was 3.2 %.

Table (1): Selected properties of corn cob biochar (CCB).

Ash %	43.5
Moisture %	3.2
pH	8
Particle size (μm)	50 - 160
Specific surface area (m^2/g)	42
Average pore size (nm)	2.7526×10^3
Total pore volume (cm^3/g)	0.0575

3.1.2. Brunauer-Emmett-Teller (BET) analysis

BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of biochar. The specific surface area, average pore size, and total pore volume of CCB are presented in Table (1). The BET surface area of CCB was found to be 42 m^2/g . If a high specific surface area exposes on the biochar surface, it brings on more interfaces to adsorb the pollutant; the large surface area plays an important role in the adsorptive properties of biochar by providing a large available space for pesticides adsorption. The accessibility of surface charges is determined by the surface area, which in turn controls the cation exchange

capacity[27]. Likewise, particle size was found to range from 50 – 160 μm , and the total pore volume (0.058 cm^3/g), the interconnectedness of the pores and porosity are important elements in determining biochar's water retaining ability[28], and the pore size of biochar is contributed to adsorb pesticides significantly[29]. The N_2 adsorption isotherms of the adsorbents are presented in Fig. (1). The adsorption isotherms are classified as type III by Brunauer, suggesting that the heat of N_2 gas adsorption on the surfaces of CCB is low[30].

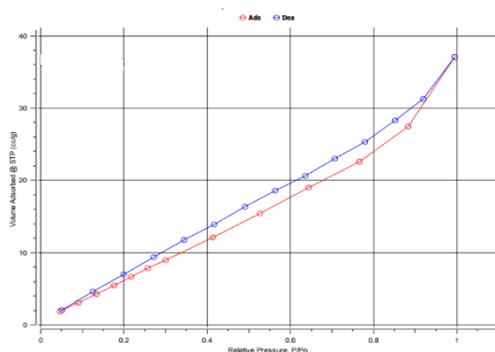


Fig. (1): The N_2 adsorption-desorption isotherms of corn cob biochar (CCB).

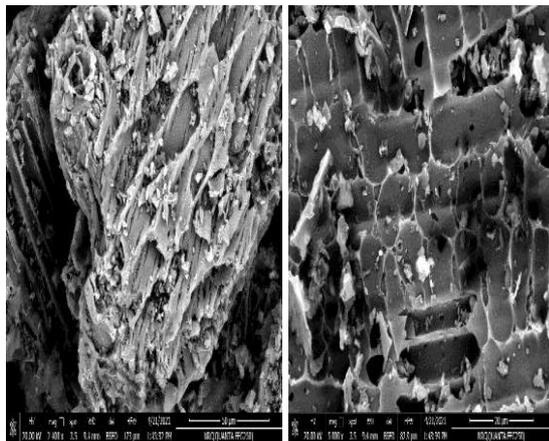


Fig. (2): SEM images of corn cob biochar (CCB).

3.1.3. Scanning electron microscopy (SEM)

SEM produces detailed and magnified images of a CCB by scanning its surface to create a high-resolution image. The surface morphology of CCB is shown in Fig. (2). The surface of the CCB became rougher and cracks appeared. During pyrolysis, more pores were generated, and the size of the pores became smaller[31]. A rich pore structure is of great value for CCB, determining its potential as an adsorbent. Hard woody materials (such as CCB) produced a spongy-like cross linked pores[32].

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3.1.4. X-ray diffraction (XRD) analysis

For characterizing crystalline materials, X-ray diffraction is a potent nondestructive technique. Structures, phases, preferred crystal orientations (texture), and other structural data such as average grain size, crystallinity, strain, and crystal defects are all included[34].

The crystalline phases generated on CCB were identified using high-angle XRD diffractograms as shown in Fig. (3). The main peak in CCB was recorded at $2\theta = 26.6$; this peak is attributed to graphite [35]. In addition to the presence of silica at $2\theta = 21.8$. Whereas a group of peaks 2θ (44.8 and 20.8) indicated the presence of cellulose[36]. The presence of these compounds helps to remove pollutants by interacting with the bonds on the surface of the pesticide.

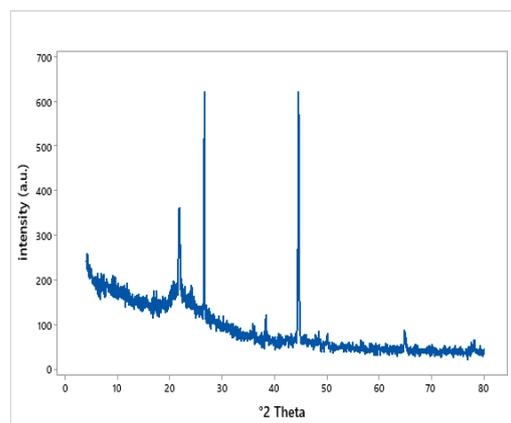


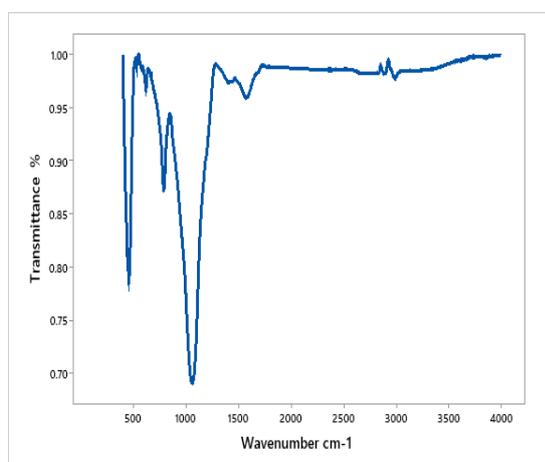
Fig. (3): X-ray diffraction (XRD) pattern of corn cob biochar (CCB).

3.1.5. Fourier transform infrared (FTIR) spectroscopy analysis

FTIR provides details about the chemical bonds and functional groups that are present in CCB, and their effects on the adsorption of a mixture of pesticides. The FTIR spectrum of the adsorbent is shown in Fig. (4). CCB shows IR spectrum with four basic band regions: weak bands between 2939 – 2830 cm^{-1} which characterize of C–H stretching represented the alkyl group (CH_3 , CH_2), indicates the presence of cellulose[36]. A broad band between 1270 and 870 cm^{-1} dedicated to the C–O stretch in ethers, alcohols, phenols, esters, and acids, is evidence for the presence of cellulose and hemicelluloses[37,38]. Weak bands between 830 and

760 cm^{-1} characterized the aromatic C–H bonding, this reveals the aromatic benzene rings existing on the adsorbent surfaces, and its appearance attributed to the presence of lignin[15,39]. Peaks between 700 – 400 cm^{-1} characterize C–C stretching[40]. According to the FTIR results, pyrolysis of the corn cob was accompanied by degradation of cellulose, hemicelluloses, and lignin, carbon condensation, and structure recombination, resulting in a decrease in the number of polar groups and an increase in the amount of aromatic carbon.

Figs. (4): The FTIR spectra of corn cob biochar (CCB).



3.2. Adsorption study

3.2.1. Effect of contact time

The effect of contact time on the removal of a mixture of ten pesticides by CCB was investigated using an initial pesticides concentration of 500 $\mu\text{g/L}$, mass adsorbent of 10 g/L , and initial pH 8, at room temperature (25 ± 0.2 $^{\circ}\text{C}$). The removal percentage of a mixture of the ten pesticides was measured at different contact times (10, 20, 30, 40, 50, 60, 80, 120, and 180 min). The order of pesticides according to their percentage of removal was as follows chlorpyrifos > ethion > cyprodinil > chlorfenvinphos > profenofos > diuron > diazinon > malathion > dimethoate > atrazine with the following removal percent: 93, 93, 92, 91, 91, 82, 70, 61, 54 and 40 % respectively.

Fig. (5-a) shows the effect of contact time on the removal efficiency of the ten pesticides. Mostly, adsorption can be split into three stages: (1) immediate adsorption; (2) sequential slow adsorption; (3) equilibrium[41]. For the pesticides mixture

studied, adsorption increased by increasing time and was fast during the initial stages before slowing down until equilibrium was attained after 60 minutes. Following this, a further increase in contact time had a slight effect on the removal of the pesticides mixture. A similar trend was also observed for pesticides adsorption onto CCB by Njoku et al., [42].

The maximum adsorption capacity of CCB under operating conditions is represented by the amount of pesticides mixture adsorbed at equilibrium. Due to the weakness of the capacity of the adsorbents, the rate of removal is controlled by transferring the particles of the pesticides mixture from outside to interior the sites between the particles of CCB. The decrease in rate over time could be attributed to the competition of pesticide molecules compared with the decreasing number of available CCB active sites. Experiments were conducted for 24 hours to ensure the equilibrium retention time. It was noted that most of the pesticides under study took a little contact time to be adsorbed on the surface of CCB; except for polar pesticides such as dimethoate and atrazine with K_{ow} 0.70 and 2.5, respectively, since they took a longer contact time compared to other pesticides. This may be due to the presence of a repulsive force between the polar groups of the polar pesticides and the negatively charged surface of CCB[43]. In addition, the sorption capacity was also related to the physicochemical characteristics of the compounds, since it increased with the hydrophobicity of the pesticides and decreased with increasing their water solubility[44]; which leads to a noticeable increase in contact time compared to less polar pesticides.

3.2.2. Effect of the adsorbent dose

As shown in Fig. (5-b), the removal percentages of the ten pesticides were increased by increasing the adsorbent dose until 20 g/L of the adsorbent. After this dose, no significant effect of the adsorbent dose was noticed. The removal efficiency of the highly polar pesticides was significantly increased by increasing the adsorbent dose from 2 to 20 g/L . For example, the removal percentage of dimethoate from the aqueous solutions increased from 11 % to 55 % when the mass adsorbent increased from 2 to 10 g/L . These results may be attributed to the competition between pesticides and water molecules to the functional groups of the surfaces of the adsorbent; when the dose of the adsorbent is increased, there is an abundance of active sites and the surface area exposed to the mixture of pesticides, which leads to reduced competition between polar pesticides and water molecules, increasing the adsorption capacity[45]. On the contrary, when the dose of

adsorbents decreases, competition increases between water molecules and polar pesticide molecules for functional groups of the adsorbent surfaces, which leads to a decrease in the rate of adsorption[46].

3.2.3. Effect of initial pH

Sorption depends heavily on pH, for instance, pH can affect both the sorbate's ionization degree and the sorbent's surface charge during the sorption process[47]. As shown in Fig. (5-c), the adsorption of most studied pesticides is enhanced by lowering the pH of the solution. Hence, the sorption of the biochar for the pesticides mixture was favored by acidic media (pH < 7), which was confirmed by previous studies[43,48]. The most pH-dependent pesticides were atrazine and dimethoate, this can be explained as follows:

Very low pH solutions will facilitate the formation of atrazine's cationic form. This may be due to its low pKa at 1.7 (weak base pesticide). Depending on the pH of the solution, these weak base molecules can be sorbed on biochar as protonated or neutral species. As a result, the presence of atrazine cations in acidic media would enhance the electrostatic attraction of pesticides to the negatively charged surface of the CCB[49]. Hence, significantly improving the adsorption of atrazine onto biochar.

For dimethoate, it is considered as one of the highest water-soluble pesticides (23.8 g/L, $K_{ow} = 0.7$) of the pesticides mixture under study, resulting in difficult removal from water compared to other pesticides, this was noticeable in this study. But with the increase in acidity (3-5), the ability of CCB to remove dimethoate increases significantly; this can be explained by the increase in the acidity of the solution, the hydroxyl groups attached to the surface increase[43]. Accordingly, increasing the acidity cause attraction of pesticides, including dimethoate.

3.2.4. Effect of initial concentration of pesticides

The effect of four initial concentrations of the pesticides mixture (200, 500, 800, and 1000 µg/L) was studied. The percentage of removal of the studied pesticides decreased with increasing the initial concentration of the pesticides. This is well illustrated in atrazine, dimethoate, and malathion, which showed less competitive sorption than others. Increasing the concentration of the pesticides is expected to saturate the adsorption sites on the surface of CCB. For example, at the initial concentration of 1000 µg/L, the removal percentage of malathion was 70 %, which increased to 93% when the initial concentration of pesticides decreased to 200 µg/L. It is clear from Fig. (5-d) that the

adsorption rate increased by decreasing pesticides concentration.

3.3. Kinetics of pesticides removal

To define the adsorption kinetics of the studied pesticides in water onto CCB two common adsorption kinetic models were used to describe the kinetic data i.e., pseudo-first order (PFO) and pseudo-second order (PSO) model. PFO and PSO kinetic parameters and R^2 for adsorption of the studied pesticides onto CCB are presented in Table 4. The PFO plots are straight lines ($\ln(q_e - q_t)$ against t), and the R^2 values were ranged from 0.89 to 0.99 which were higher than those of the PSO. Therefore, the best-fit model of experimental data was the PFO model which suggests that pesticides adsorption onto CCB is more inclined toward physisorption interactions, and the adsorption process depends on the initial concentration of pesticides. Kinetic data modeling exhibited the contribution of physisorption, via pore diffusion, $\pi^*-\pi$ electron donor-acceptor interaction, H-bonding, and van der Waals dispersion forces[25,50]. Physical properties such as surface area, pore size, and surface functional groups found in CCB, which promote pesticide adsorption on the adsorbents' surfaces, shape these forces[51]. Similar results have been reported for the adsorption of carbofuran pesticide by tea waste and rice husks[50].

3.4. Adsorption isothermal models

Adsorption isotherm was used to reflect the relationship between the amount of pesticides and their concentration in the equilibrium solution. In such experiments, the experimental sorption data are often analyzed using the Langmuir and Freundlich models, which correspond to the homogenous and heterogeneous sorbent surfaces, respectively. The Langmuir and Freundlich parameters are shown in Table (5). The Langmuir isotherm model shows the best fit compared to the Freundlich model for the adsorption of the ten pesticides by CCB at the experimental conditions; because the R^2 of the Langmuir ranged from 0.957 to 0.999 which was higher than that of the Freundlich model that ranged from 0.83 to 0.99. The Langmuir isotherm assumed that the adsorption took place only at homogenous sites within the CCB surface with uniform energy level, this demonstrated that pesticides mixture adsorption onto CCB followed monolayer adsorption [19]. Similar trends in many previous studies of pesticide removal from water by biochar fit the Langmuir model [32,47,52,53].

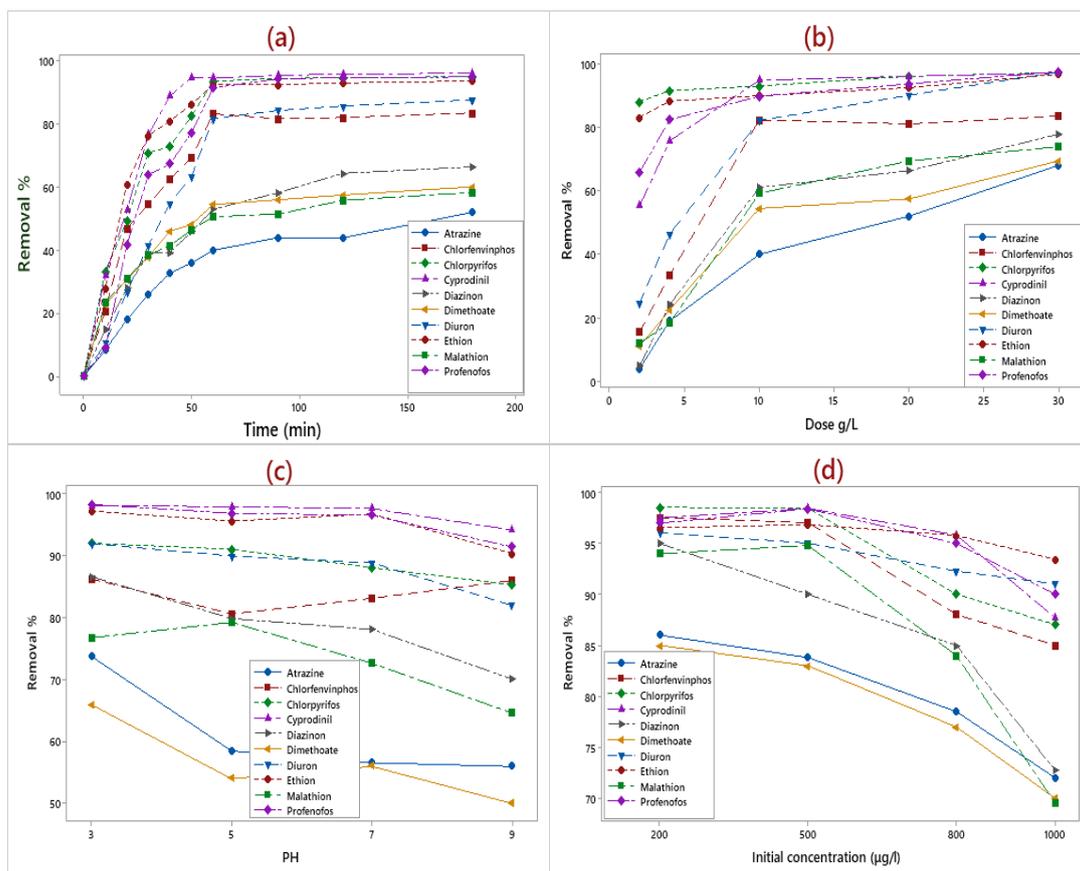


Fig. (5): Effect of (a): contact time, (b): initial dose of CCB, (c): initial pH, and (d): initial concentration of pesticides on the removal efficiency of the ten pesticides by corn cob biochar (CCB).

Table 4: Kinetic parameters for the adsorption of a mixture of ten pesticides onto corn cob biochar (CCB).

Pesticide	Pseudo-first order			Pseudo-second order		
	q_e ($\text{mg} \cdot \text{g}^{-1}$)	K_1 (min^{-1})	R^2	q_e ($\text{mg} \cdot \text{g}^{-1}$)	K_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	R^2
Atrazine	0.056	-2.5E-04	0.96	0.011	0.076	0.81
Chlorfenvinphos	0.050	-5.8E-04	0.89	0.006	0.345	0.84
Chlorpyrifos	0.073	-7.2E-04	0.92	0.008	0.223	0.81
Cyprodinil	0.091	-7.1E-04	0.90	0.005	0.354	0.91
Diazinon	0.062	-4.0E-04	0.99	0.010	0.108	0.83
Dimethoate	0.052	-1.7E-04	0.96	0.252	0.002	0.03
Diuron	0.093	-5.7E-04	0.97	0.025	0.039	0.48
Ethion	0.053	-5.5E-04	0.97	0.004	0.576	0.97
Malathion	0.068	-3.2E-04	0.94	0.015	0.053	0.87
Profenofos	0.046	-7.2E-04	0.94	0.003	1.738	0.99

Table 5: The Langmuir and Freundlich constants for the adsorption of ten pesticides on corn cob biochar (CCB).

Pesticide	Langmuir model				Freundlich model			Removal%
	Q (mg/g)	b (L/mg)	R _L	R ²	1/n	k _f (mg/g)	R ²	
Atrazine	0.03478	3.9741	0.3348	0.999	0.49	0.03	0.988	85
Chlorfenvinphos	0.06069	40.551	0.0470	0.999	0.31	0.08	0.976	96.3
Chlorpyrifos	0.08102	51.489	0.0374	0.986	0.29	0.12	0.999	97.6
Cyprodinil	0.09464	69.974	0.0278	0.995	0.39	0.21	0.964	98.0
Diazinon	0.04345	14.618	0.1204	0.957	0.47	0.06	0.914	90.8
Dimethoate	0.09122	2.8529	0.4121	0.99	0.66	0.09	0.996	83.5
Diuron	0.0775	23.107	0.0797	0.992	0.40	0.12	0.971	95
Ethion	0.11341	25.485	0.0728	0.969	0.54	0.29	0.992	96.5
Malathion	0.03046	41.778	0.0457	0.984	0.19	0.03	0.940	94.5
Profenofos	0.0998	52.681	0.0366	0.998	0.46	0.26	0.925	97.5

Moreover, results demonstrated that R_L values were less than 1 which illustrated favorable adsorption of CCB for all tested pesticides. The R_L value < 1 was also reported on the 2,4-D adsorption onto switchgrass biochar and CCB [15,54].

Conclusions

In this work, the ability of CCB as effective and low-cost agricultural waste adsorbent material to remove the ten pesticides from aqueous solutions was examined. The adsorption equilibrium was achieved after 60 min. The pH was a key factor for the mixture of pesticides removal on CCB. The sorption capacity of CCB was markedly increased at pH 3; increasing pH and deprotonation may be responsible for its ineffectiveness. The sorption of the tested pesticides to CCB is dependent on the hydrophobicity of each pesticide; it has been observed that the highly hydrophobic (K_{ow}) pesticides show higher adsorption on the CCB, such as (chlorfenvinphos, chlorpyrifos, cyprodinil diazinon, diuron, ethion, and profenofos), while the adsorption of highly polar pesticides such as (atrazine, dimethoate, and malathion) requires longer adsorption times because the water molecules compete for the polar functional groups of the CCB.

The adsorption kinetic data were better represented by the pseudo-first order model. The equilibrium adsorption data were analyzed, and results indicated that Langmuir model agrees with the data well. Residues of the pesticide mixture were determined by direct injection using LC-MS/MS, and the run time of the HPLC method was 4 minutes. This study has successfully proved, that the corn cob

biochar can be used as an eco-friendly, economic sorbent in the removal of pesticides mixture from water.

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