ACS OMEGA

Open Access

This article is licensed under CC-BY 4.0

http://pubs.acs.org/journal/acsodf

Article

Impact of Natural Organic Matter Competition on the Adsorptive Removal of Acetochlor and Metolachlor from Low-Specific UV Absorbance Surface Waters

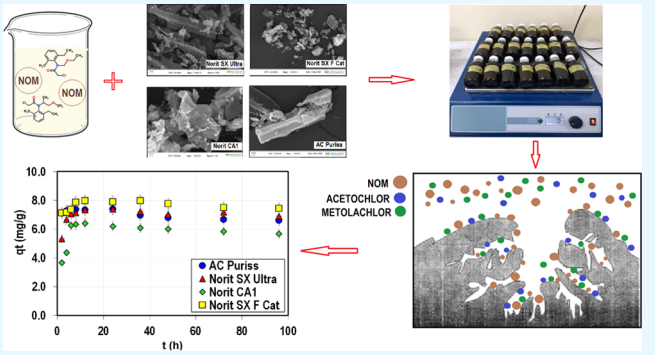
Emine Yilmaz, Ezgi Altiparmak, Filiz Dadaser-Celik, and Nuray Ates*

Cite This: *ACS Omega* 2023, 8, 31758−31771

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Although activated carbon adsorption is a very promising process for the removal of organic compounds from surface waters, the removal performance for nonionic pesticides could be adversely affected by co-occurring natural organic matter. Natural organic matter can compete with pesticides during the adsorption process, and the size of natural organic matter affects the removal of pesticides, as low-molecular-weight organics directly compete for adsorbent sites with pesticides. This study aims to investigate the competitive impact of low-molecular-weight organics on the adsorptive removal of acetochlor and metolachlor by four commercial powdered activated carbons. The adsorption features of selected powdered activated carbons were evaluated in surface water samples collected from the influent stream of the filtration process having 2.75 mg/L organic matter and 0.87 L/mg-m specific UV absorbance. The adsorption kinetics and capacities were examined by employing pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models and modified Freundlich and Langmuir isotherm models to the experimental data. The competitive removal of acetochlor and metolachlor in the presence of natural organic matter was evaluated for varied powdered activated carbon dosages on the basis of UV and specific UV absorbance values of adsorbed organic matter. The adsorption data were well represented by the modified Freundlich isotherm, as well as pseudo-second-order kinetics. The maximum organic matter adsorption capacities of the modified Freundlich isotherm were observed to be 120.6 and 127.2 mg/g by Norit SX Ultra and 99.5 and 100.6 mg/g by AC Puriss for acetochlor- and metolachlor-containing water samples, respectively. Among the four powdered activated carbons, Norit SX Ultra and AC Puriss provided the highest natural organic matter removal performances with 76 and 72% and 71 and 65% for acetochlor- and metolachlor-containing samples, respectively. Similarly, Norit SX Ultra and AC Puriss were very effective for adsorbing aromatic organics with higher than 80% specific UV absorbance removal efficiency. Metolachlor was almost completely removed by higher than 98% by Norit SX Ultra, Norit SX F Cat, and AC Puriss, even at low adsorbent dosages. However, an adsorbent dose of 100 mg/L and above should be added for all powdered activated carbons, except for Norit SX F Cat, for achieving an acetochlor removal performance of higher than 98%. The competition between low-molecular-weight organics (low-specific UV absorbance) and acetochlor and metolachlor was more apparent at low adsorbent dosages (10−75 mg/L).



Downloaded via ERCIYES UNIV on September 6, 2023 at 10:58:49 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

1. INTRODUCTION

Pesticides are blends of organic and synthetic compounds, employed to combat insect pests, vectors, and weeds in household, industrial, agricultural, and other public areas[1] as well as to increase the quality and quantity of products in agricultural activities.[2] Pesticide concentrations in water resources are associated with crop type and density, as well as agricultural management techniques in the watershed.[3] Previous studies on pesticide occurrence have shown that surface water resources in developing countries have substantially higher pesticide concentrations and carry a wider variety of pesticides than developed countries.[4] Acetochlor and metolachlor, known as chloroacetanilides, are the most commonly used herbicides for corn, cotton, rice, soybean, sugar cane, sugar beet, and sunflower production to control broadleaf weeds and annual grasses. As they are relatively water-soluble, have lower volatility, are resistant to degradation, and are persistent in the environment, they are frequently identified in water and soil throughout the world.[5−7]

Received: April 24, 2023
Accepted: August 8, 2023
Published: August 18, 2023



© 2023 The Authors. Published by American Chemical Society

While acetochlor is listed as a B-2 carcinogen and a thyroid disrupter,[7] metolachlor has toxic effects on the kidney, liver, and cardiovascular and nervous systems.[8,9] It is anticipated that up to 96% of surface waters located close to agricultural activities contain detectable amounts of acetochlor as a result of transport and conversion mechanisms.[10] In monitoring studies conducted in 38 rivers in the United States, 8 of the top 10 most detected organic chemicals were pesticides, including metolachlor.[11]

The first legislative action on pesticides, named the Federal Insecticide, Fungicide, and Rodenticide Act, was issued in 1947 in the United States,[12] and federal standards were set for only 22 pollutants after updating the regulation in 1986 and 1996. This act required the nationwide monitoring of linuron, metolachlor, cyanazine, and metribuzin, among many pollutants. Three pesticides, including alachlor, metolachlor and their metabolites, and acetochlor, were included in the monitoring program in 2009.[13] The European Council has identified 45 priority substances/substance groups in the Water Framework Directive based on research data on short- and long-term effects on the aquatic living organisms and human health, which include 12 organochlorine and 3 organophosphorus pesticides.[14] The regulation of Surface Water Quality Management in Turkey defined Environmental Quality Standards for 250 pollutants; of which 45 were covered within the priority substance list. 19 pesticides were present in the list.[15]

Pesticide removal from water is primarily influenced by pesticide characteristics (solubility, polarity, volatility, acidity, lipophilicity, etc.), water characteristics (organic matter content, pH, type, and concentrations of background ions, temperature, etc.), and treatment techniques.[16] For effective pesticide removal from water and wastewater, advanced treatment methods, such as adsorption, ion exchange, membrane filtration, advanced oxidation processes, and their hybrid combinations are recommended.[17−19] Adsorption is considered a promising process for pesticide removal, since it is well-known, low-cost, and very effective. Several natural and commercial adsorbents are available as well as modified and functionalized adsorbents have been developed for removing toxic and micropollutants, including pesticides.[20−23] Still, powdered activated carbon (PAC) remains the widely used adsorbent for pesticide removal because it is low-cost and easily available, it can be added when needed, its dosage can be adjusted easily according to pollutant concentration changes, it does not require a separate reactor, and it can be removed by precipitation or filtration processes after its use.[20]

The occurrence of natural organic matter in water sources can pose challenges to the effective removal of pesticides. It is considered that natural organic matter (NOM) in various molecular weights has different competitive impacts on micropollutant removal by the adsorption process from water sources, and in general, low-molecular-weight organics, which cannot be removed by coagulation, show the highest competition during micropollutant removal.[24−29] The size of NOM affects the adsorption efficiency of micropollutants by decreasing the adsorbent capacity. While low-molecular weight NOM compete for direct sites, high-molecular weight NOM cause pore entrance blockage. In the removal of micropollutants by activated carbon adsorption, the dominant competitor for the active sites of the adsorbent is NOM with a molecular weight of less than 600 g/mol in natural waters, and low-molecular-weight organics compete with micropollutants by blockage of the micropores of the adsorbent. On the other hand, the effects of competitive and pore blockage of NOM might be less significant for mesoporous-activated carbons.[30] Depending on the characteristic of NOM specific to the water source and the pore size distribution and size of activated carbon, the degree of the competitive effect of NOM against micropollutants can be different. Specific UV absorbance (SUVA) represents the numerical quantity of aromatic content and the humic fraction, since the aromatic structure of NOM containing conjugated C=C double bonds absorbs UV light at 254 nm. SUVA normalized by dividing UV_{254} by the dissolved organic carbon (DOC) value is widely used as a surrogate parameter of predominant organic compounds for water-containing NOM mixtures.[31,32] When the SUVA value is lower than 2 L/mg-m, water sources in terms of NOM are defined as having non-humic, mostly aliphatic, lower-molecular-weight fractions and hydrophilic compounds and are characterized as low-SUVA waters.[33−35]

There are a few studies on the removal of acetochlor and metolachlor from water and wastewater by activated carbon using synthetic model waters or real waters. In the majority of these studies, acetochlor or metolachlor concentrations ranged between 10 and 100 mg/L, much higher than those expected in surface waters.[36−40] Although competition between NOM and pesticides would be expected in the adsorption process, only few studies investigated the impact of organic characteristics on the nonionic pesticide (e.g., acetochlor and metolachlor) removal mechanism.[26−28] The main objective of this study is to investigate the competitive removal of acetochlor and metolachlor from surface waters in the presence of low-molecular-weight NOM with hydrophilic characteristics by four different powdered activated carbons (PACs). The water samples used in this study were collected from the influent stream of the filtration process and had 2.75 mg/L NOM (in terms of DOC), 0.024 cm^{-1} UV_{254}, and 0.87 L/mg-m SUVA. Among the PACs, one was steam-modified and the other one was chemically modified. The other two were untreated. In the scope of the study, the adsorption kinetics and capacities for selected PACs were determined as well as the removal performances of acetochlor, metolachlor, and NOM were evaluated.

2. MATERIAL AND METHODS

2.1. Water Samples and Chemicals. The water samples were collected from the influent stream of the filtration process in the Konya Water Treatment Plant (Turkey) in April 2021. The Konya Water Treatment Plant receives water from the Altinapa Reservoir and supplies drinking water to the city of Konya with 2.5 million population. In previous studies, acetochlor and metolachlor were identified at levels higher than the Environmental Quality Standards provided in the regulation of Surface Water Quality Management in Turkey.[15,41] Water samples collected were carried to the laboratory in 25 L cooled jerricans and kept at +4 °C in a fridge for experimental studies. The properties of the water samples are presented in Table 1.

Acetochlor (Cat. No. Supelco 33379) and metolachlor (Cat. No. Supelco 36163) analytical standards (≤100% purity) were supplied from Sigma-Aldrich. The major properties of the tested pesticides are shown in Table 2. The chemicals (chloroform, acetone, methanol, and acetonitrile) used in pesticide analysis were HPLC/GC grade and obtained from Merck (Merck, Darmstadt, Germany).

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771

Table 1. Physicochemical Properties of Water Samples

parameter	value[a]
pH	7.85
electrical conductivity (μS/cm)	367
total hardness (mg$CaCO_3$/L)	210
alkalinity (mg$CaCO_3$/L)	201
UV_{254} (1/cm)	0.024
dissolved organic carbon (DOC) (mg/L)	2.75
total nitrogen (TN) (mg/L)	1.50
specific UV absorbance (SUVA) (L/mg-m)	0.87

[a]The values for parameters are the average of three measurements.

2.2. Adsorbents. In adsorption experiments, four different PACs, Norit SX Ultra (Cat. No. 53663), Norit CA1 (Cat. No. 97876), Norit SX F Cat (Cat. No. 901933), and AC Puriss (Cat. No. 31616), obtained from Sigma-Aldrich, were used. While Norit SX Ultra and Norit CA1 were originally steam- and chemically modified, respectively, the other two activated carbons were originally untreated. The adsorbents were characterized in terms of particle size distribution, surface chemistry (point of zero charge (pH_{pzc}), total acidic and basic groups, functional groups), surface area, and morphology.

2.3. Experimental Procedure: Kinetic and Isotherm Adsorption Tests. Adsorption testing was performed in two stages: (1) kinetic tests were applied to determine the time to equilibrium and (2) equilibrium tests were applied to assess adsorption capacities. Kinetic tests were accomplished at a 300 mg/L constant adsorbent dose in 100 mL of water samples in amber glass bottles with a PTFE cap in two sets containing 500 μg/L either acetochlor or metolachlor. In order to identify the equilibrium time, the samples were thoroughly mixed at 120 rpm on a shaker in a horizontal position for 2, 4, 8, 12, 24, 36, 48, and 72 h. In equilibrium experiments, 100 mL of water samples, to which PACs were added at 10 different doses, ranging from 10 to 1000 mg/L, were prepared in two sets containing 500 μg/L either acetochlor or metolachlor and were thoroughly shaken horizontally at 120 rpm at a temperature of 25 ± 2 °C. The pHs of all samples were set to 8 ± 0.1 with K_2HPO_4 and KH_2PO_4 buffer solutions. After a certain contact time, which had been previously determined in kinetic tests, the PACs were separated from samples by 0.45 μm filter paper and kept in the fridge until further analytical tests. The filter paper had previously been washed with distilled water (500 mL) to avoid possible organic leaks from the filter. Acetochlor, metolachlor, DOC, UV absorbance, pH, and conductivity analyses were employed on water samples obtained from kinetic and isotherm tests. All tests were conducted in two parallels; all parameters were analyzed three times, and the averaged data were presented. Control samples without activated carbon were also included in all isotherm experiments. DOC values were used to evaluate kinetic types and rates and adsorption capacities of PACs, since the NOM content of the samples was relatively higher, and they had higher competition against adsorbents than pesticides.

The adsorption capacity (NOM absorbed on PACs) was calculated by dividing the difference between the initial and final adsorbate concentrations by the adsorbent dose, given in eq 1.

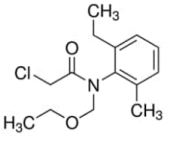
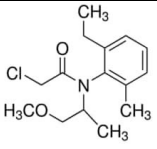
$$q = \frac{(C_0 - C)V}{M} \quad (1)$$

In eq 1, C_0 and C represent the initial and final quantities of organic matter in the aqueous phase (mg/L), respectively. Adsorption capacity (mg/g), sample volume (L), and mass of PACs (g) are indicated by q, V, and M, respectively.

The linear forms of three common kinetic models, including the pseudo-first-order model (PFO), pseudo-second-order model (PSO), and intraparticle diffusion model (IPDM), were adapted to the kinetic data. The linearized PFO and PSO models are given in eqs 2 and 3.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (2)$$

Table 2. Properties of Acetochlor and Metolachlor

Properties	Pesticides[a]	
	Acetochlor	Metolachlor
Molecular Structure		
Linear Formula	$C_{14}H_{20}ClNO_2$	$C_{15}H_{22}ClNO_2$
Molecular Weight (g/mol)	269.77	283.79
Solubility in water @ 25 °C (mg/L)	233	488
Surface Area (Å^2)	244.9	265.0
Topological Polar Surface Area (Å^2)	29.5	29.5
logK_{ow}	4.14	3.13
Henry's Constant @ 25 °C (atm- m^3/mol)	$2.66*10^{-10}$	$2.44*10^{-8}$
Environmental Quality Standards (Max) (µg/L)[b]	10.1	88

[a]The properties of pesticides were provided from https://pubchem.ncbi.nlm.nih.gov/.[42] [b]The regulation of Surface Water Quality Management in Turkey.

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771

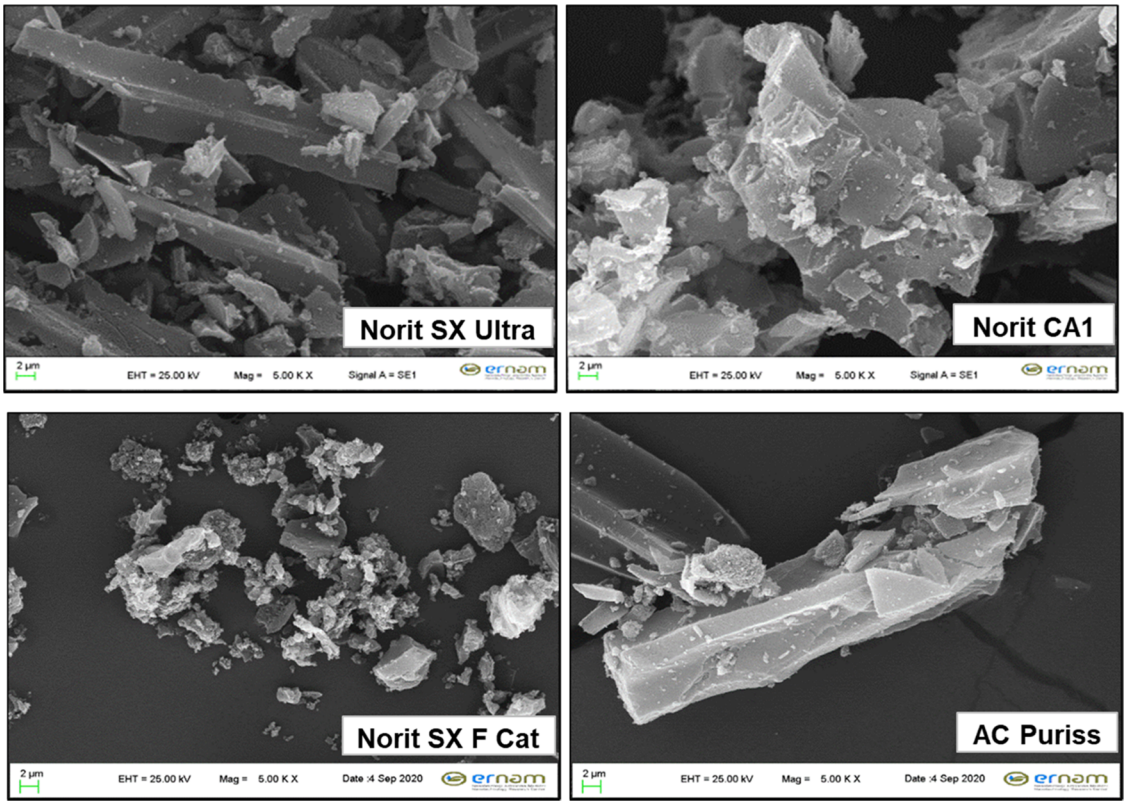


Figure 1. SEM images of activated carbons (2 μm mag: 500k×).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

In eqs 2 and 3, k_1 (1/h) and k_2 (g/mg-h) are the rate constants of PFO and PSO kinetic models, respectively; q_t and q_e are the adsorption capacities (mg/g) at time t and equilibrium, respectively.

The IPDM, proposed by Weber and Morris,[43] has been extensively applied to interpret the rate-limiting step of the adsorption process and defined as follows (eq 4)

$$q_t = k_i t^{1/2} + C \quad (4)$$

Here, q_t is the adsorption capacity at time t (mg/g), k_i is the pore diffusion parameter (mg/g-h$^{1/2}$), t is the contact time, and C is an arbitrary constant (mg/g).

2.4. Analytical Methods. Acetochlor and metolachlor were analyzed by a Shimadzu LC-2030C HPLC, equipped with a GL Sciences Inertsil ODS-4 (particle size: 5 μm, length: 250 mm, i.d: 4.6 mm column, GL Sciences), and a UV detector. Calibration standards and water samples containing acetochlor and metolachlor were extracted using the dispersive liquid−liquid microextraction (DLLME) technique before HPLC analysis. For the quantitative analysis of pesticides, an 8-point calibration curve was used using standard samples prepared from acetochlor and metolachlor standard mixtures. In the extraction procedure, 1,2-dichloroethane (400 μL) and acetonitrile (1 mL) extraction−dispersive solvent mixtures for acetochlor and 1,2-dichloroethane (300 μL) and methanol (1 mL) extraction−dispersive solvent mixtures for metolachlor were added to either calibration solutions or water samples (8 mL). In the extraction procedure, the samples were first vortexed for 1 min and later centrifuged at 6000 rpm for 2.0 min, and finally, the separated organic phases were taken into vials containing 100 μL inserts to be analyzed by the HPLC instrument at wavelengths of 210 nm for acetochlor and 230 nm for metolachlor. The limit of detection (LoD) and limit of quantification (LoQ) levels were 0.89 and 2.71 μg/L for acetochlor and 1.17 and 3.54 μg/L for metolachlor, respectively. The amount of NOM in terms of DOC was determined according to SM 5310 B[44] with a TOC analyzer (TOC-L CPH, Shimadzu) after the samples were filtered through a 0.45 μm filter. A-6 point calibration standards were prepared for concentrations ranging from 0.2 to 6 mg/L with potassium hydrogen phthalate. A UV−visible spectrophotometer (Hach Lange DR 6000) was used to measure the UV absorbance of water samples at a wavelength of 254 nm according to the SM 5910 B method.[44] Conductivity (SM 2510) and pH were measured (SM 4500-H$^+$) by a Hach (HQ40d) multimeter.

The surface chemistry of PACs is characterized by acid and base neutralization capacities, which are neutral charge points (pH_{pzc}). The pH_{pzc} values of the activated carbon samples were attained in compliance with the method of Dastgheib et al.[45] The pH values of a 0.1 M NaCl solution prepared in pure water were adjusted in 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 with 0.5 M HCl and/or 0.5 M NaOH. 20 mL of the sample was mixed by adding 100 mg of the adsorbent at 100 rpm and 20 ± 5 °C for 48 h. The pH_{pzc} value of the samples is equal to the initial pH value, and no change is observed during the contact period after the adsorbent is added. Total surface acidic and total surface basic groups were determined by applying the Boehm method (alkalimetric titration) with minor modification of modifications in the method by Dastgheib et al.[45] A series of 20 mL of 0.05 N NaOH or 0.05 N HCl solutions containing 200 mg of adsorbents were mixed at room

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771

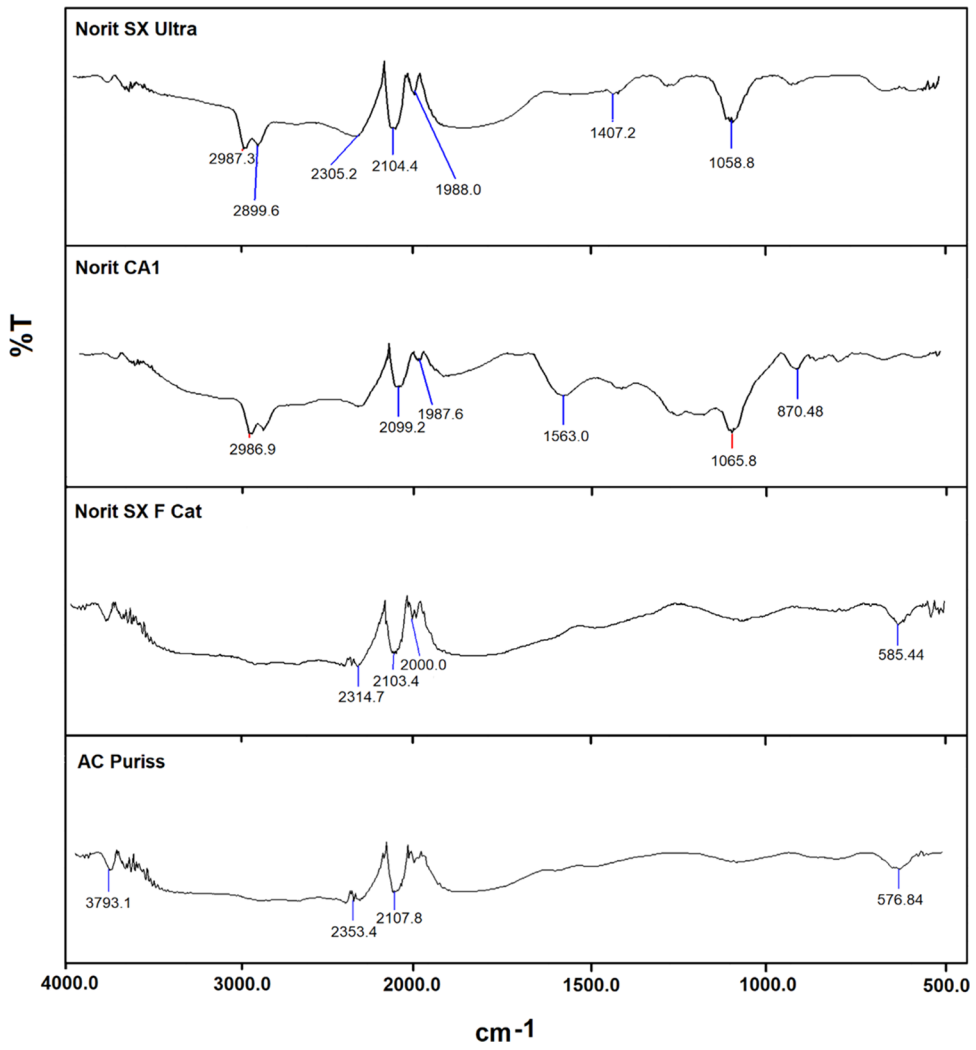


Figure 2. FTIR spectra of tested PACs.

temperature at 100 rpm for 48 h. Additional blank samples without adsorbents were also included in the test. At the end of contact time, the samples were left for 4 h for precipitation of the adsorbents and then filtered. 10 mL of the filtered samples were titrated with either 0.05 N HCl or 0.05 N NaOH. The differences in the spent amount of HCl/NaOH for the blank and adsorbent-containing samples were used to calculate the total surface acidic and basic groups.

Surface areas (BET) and total pore volumes of the adsorbents were determined with a Micromeritics Gemini VII Surface Area and Porosity Surface Analyzer. FTIR analyses of adsorbents were carried out by a Perkin Elmer 400 FT-IR/FT-FIR device in the wavelength range of 400−4000 cm^{-1}. The particle size distribution of the adsorbents was determined by dynamic light scattering (DLS) analysis. DLS parameters of PACs were determined using a Malvern NanoZS90 instrument equipped with a 633 nm laser at ambient temperature. Data were collected with a scattering angle of 173°. BET, FTIR, and DLS analyses were performed at the Erciyes University Technology Research and Application Center.

3. RESULTS AND DISCUSSION

3.1. Characterization of Adsorbents. Particle sizes of the adsorbents were determined by the weighted average calculation method using DLS histograms. The particle sizes of Norit SX Ultra were distributed between 190 and 1718 nm, with a mean size of 379 nm. Approximately 80% of the particles had particle sizes within the range of 190 and 396 nm. The mean particle size of Norit CA1 was 685 nm, and about 80% of particles were between 396 and 955 nm. Although the average particle size of Norit SX F Cat was 938 nm (255−6439 nm), about 55% of the particles had sizes below 955 nm. On the other hand, AC Puriss had an average particle size of 253 nm and its particle sizes ranged from 122 to 3091 nm, while 85% of the particles were smaller than 295 nm. The SEM images of the adsorbents at 2 μm size and a 500k× magnification scale are given in Figure 1. For all PACs, the apparent porosity can be seen from images. The particles of Norit SX Ultra and AC Puriss were mostly in finger shape, while the particles of Norit CA1 and Norit SX F Cat were in distorted spherical form. Besides, the particle size distribution of Norit SX Ultra and Norit SX F Cat had a wider range, which can also be seen in SEM images.

The FTIR spectra for Norit SX Ultra, Norit CA1, Norit SX F Cat, and AC Puriss are presented in Figure 2. There are three and four major bands observed for Norit SX F Cat and AC Puriss adsorbents, respectively. The transmission in the range of 450−750 cm^{-1} is attributed to the aromatic ring deformation, and 585 and 576 cm^{-1} absorption bands correspond to C−H bending mode.[46] The vibrations at 2000

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771

cm^{-1} correspond to the C═C═N stretch of ketenimine; those at 2103 and 2107 cm^{-1} indicate the C≡C stretch of alkyne groups, and the signals at 2314 and 2353 cm^{-1} may represent ketone groups and the vibration of the −COOH structure for Norit SX F Cat and AC Puriss adsorbents.[47−49]

On the other hand, six signals were detected for Norit SX Ultra and Norit CA1. The vibration at 870 cm^{-1} indicates the existence of strong C−H bending. The presence of C−O stretching vibrations in alcohols, phenols, acids, ethers, or esters is indicated by the absorption at 1058 and 1065 cm^{-1}. While the 1407 cm^{-1} absorption band can be attributed to the O−H bond of carboxylic acid or alcohol[50] and O═C−O belonging to the −COOH groups.[7,51] The C═C stretching vibration in aromatic rings, specifically containing NO_2 groups, is responsible for the peak at 1563 cm^{-1}.[47,52] The C═C═N stretch of ketenimine groups was observed between 1987 and 1988 cm^{-1}. The symmetric and asymmetric C−H stretching vibrations of aliphatic acids are supposed to be responsible for the peaks of 2899, 2986, and 2987 cm^{-1}.[53]

The average BET area, total pore volume, pore diameter, pH_{pzc}, and total acidic and basic groups of the adsorbents are given in Table 3. The surface areas and pore sizes of the

Table 3. Physical and Chemical Characteristics of Activated Carbons

adsorbent		Norit SX Ultra	Norit CA1	Norit SX F Cat	AC Puriss
BET surface area S_{BET} (m^2/g)		1200	1161	657	274
total pore volume (cm^3/g)		0.95	1.12	0.78	0.22
average pore diameter (nm)		3.16	3.86	4.75	3.24
pH_{PZC}		8.11	2.53	7.8	7.09
total acidic groups	(meq/g)	3.6	4.0	3.5	3.8
	(meq/m^2)	0.003	0.003	0.005	0.014
total basic groups	(meq/g)	3.33	3.03	3.8	3.9
	(meq/m^2)	0.003	0.003	0.006	0.014

adsorbents were attained from N_2 adsorption−desorption isotherms based on the nitrogen (N_2) gas adsorption technique in a liquid nitrogen environment at 77 K. The N_2 adsorption−desorption isotherms of all adsorbents more likely conform to the Type IV isotherm curve of mesoporous materials according to the IUPAC classification, which represents the layer-by-layer adsorption of mesoporous materials on a smooth non-porous surface. While Norit SX Ultra and Norit CA1 had similar BET average surface areas of 1200 and 1161 m^2/g, respectively, AC Puriss had the lowest surface area of 274 m^2/g.

The pH_{pzc} value shows that the adsorbent surface would be positively or negatively charged based on the pH of the water samples. At pH values lower than pH_{pzc}, the surface of the adsorbent is mostly positively charged, while at higher pH values, it is negatively charged. As shown in Table 3, with a pH_{pzc} value of 7.8, the surface of Norit SX F Cat was neutral, since the pH of the water sample was 7.85 (Table 1). The pH_{pzc} values for Norit SX Ultra and AC Puriss were determined as 8.11 and 7.09, implying that the surfaces of adsorbents were slightly positively and negatively charged in the solution, respectively. On the other hand, the surface of Norit CA1, having the lowest pH_{pzc} value of 2.53 (pH ≫ pH_{pzc}), would be strongly negatively charged. The strong O−H stretching of 2986.9 cm^{-1} belonging to carboxyl groups and strong C−O stretching of 1065.8 cm^{-1} belonging to primary alcohols might be responsible for the negatively charged surface of Norit CA1.[48,54] The amount of total surface acidic and basic groups identified by the Boehm method also supported this phenomenon that having higher acidic groups resulted in lower pH_{pzc} values.[55]

3.2. Effect of Contact Time. The equilibrium times for organic matter (in terms of DOC) adsorption onto activated carbons were evaluated, and the results are presented in Figure 3. As mentioned earlier in Section 2, since the concentrations

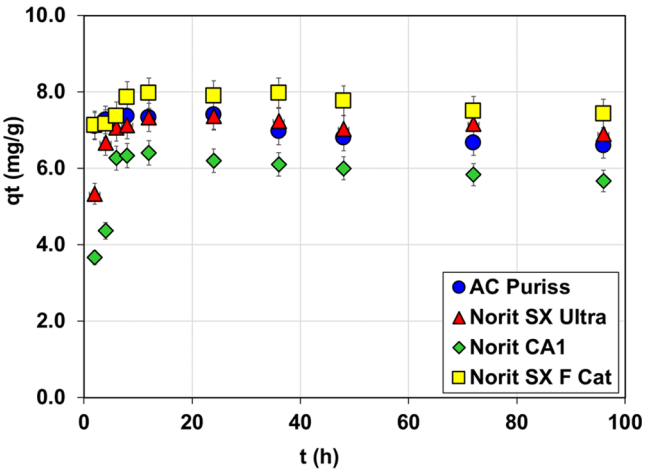


Figure 3. Adsorption capacities of PACs versus time (pH: 7.85, C_0: 2.75 mg/L, T: 25 °C, m: 300 mg/L, stirring at 120 rpm).

of acetochlor and metolachlor in the samples are very low compared to the amount of organic matter and there is significant competition between them, the adsorption kinetic and isotherm models were investigated on the basis of organic matter. Adsorption of organic matter by adsorbents occurred very rapidly in the first few hours within the 96 h contact time. Especially AC Puriss and Norit SX F Cat carbons reached the equilibrium plateau within the first 6 h. On the other hand, the equilibrium plateau for Norit SX Ultra and Norit CA1 carbons was gradually attained after 10−12 h. When the adsorption equilibrium phase was reached, the lowest and the highest DOC removal performances were obtained with 60 and 75% on average by the Norit CA1 and Norit SX F Cat activated carbons, respectively. Besides, on average, 70% DOC removal was observed for AC Puriss and Norit SX Ultra adsorbents. In previous studies, the time for adsorbents to reach equilibrium in the removal of organic materials and/or pesticides with activated carbon is identified as between 0.5 h and 7 days.[56,57]

Adsorption of NOM by PAC is a complex phenomenon, as it is a complex heterogeneous combination of humic acids, fulvic acids, low-molecular-weight organic acids, carbohydrates, proteins, and other components. Therefore, different mechanisms such as hydrophobic effect, electrostatic interactions, hydrogen bonding, and $\pi-\pi$ bonds are effective during the adsorption of NOM on the PAC in the aqueous phase.[58] Electrostatic interactions predominate in adsorbing NOM, which is generally negatively charged in surface waters, by positively charged PAC; on the other hand, the pore size of adsorbents is the primary control factor for NOM adsorption.[59] As seen from Figure 3, all PACs provided similar adsorption behavior in terms of NOM adsorption from aqueous solution, even though they have a wide range of pH_{pzc} values (2.53−8.11). However, the slower adsorption rate

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771

(in early contact times) and capacity of Norit CA1 with respect to others is due to its strongly negative charges repelling NOM compounds. Norit SX F Cat and AC Puriss were neutral or slightly negatively charged at 7.85 pH of the water sample, and it was assumed that their pore sizes of 4.75 and 3.24 nm were primary control factors for NOM adsorption, respectively. Besides, the oxygen-containing functional groups on the structure of Norit SX F Cat and AC Puriss might have a dominant role by making H-bonds between NOM moieties and adsorbents.[58]

3.3. Adsorption Kinetic Models. Since their accurate depiction of the actual data, pseudo-kinetic models, which simulate the total rate of adsorption, are commonly used for modeling the kinetics of adsorption processes.[60,61] The PFO plot with $\ln(q_e - q_t)$ plotted against t and the PSO plot with t/q_t plotted against t for determining the organic matter adsorption kinetic rates are shown in Figure 4. The kinetic

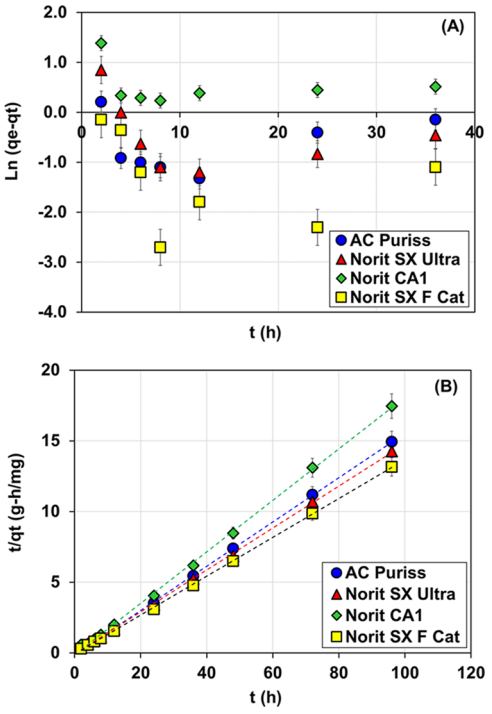


Figure 4. Pseudo-first-order kinetic (A) and pseudo-second-order kinetic (B) models for NOM adsorption by tested PACs (pH: 7.85, C_0: 2.75 mg/L, T: 25 °C, m: 300 mg/L, stirring at 120 rpm).

results obtained from the water samples containing acetochlor and metolachlor were relatively similar, and since the differences between kinetic rates and coefficients for both models were less than 5%, the average results for the kinetic parameters for these two data sets were given. The data from the kinetic experiments were better explained by PSO, having a higher R^2 with 0.99 for all activated carbons, as shown in Table 4. In addition, the predicted equilibrium capacity for the PSO kinetic model ($q_{e,calc}$) corresponded more closely to the experimental equilibrium capacity ($q_{e,exp}$) than it was for the PFO kinetic model (Table 4). Based on the PSO model results, it might be concluded that the ratio between the square of the number of vacant sites on the adsorbents and the occupancy rate of adsorption sites was linear.[62] In addition, the better fit of data to the PSO model than that to the PFO model can be attributed to chemical absorption processes, such as hydrogen bonds and $\pi-\pi$ interactions, which may be more dominant in the adsorption of organic matter to the adsorbent.[7,63,64]

The PSO rate constant (k_2) and initial sorption rate (H) for the adsorbents tested in this study displayed various ordering. The rate constants (k_2) of the PSO model and the initial sorption rate constants (H) followed the order of Norit SX Ultra > Norit SX F Cat ≥ Norit CA1 > AC Puriss and Norit SX Ultra > Norit SX F Cat > AC Puriss ≥ Norit CA1, respectively. Indeed, Norit SX Ultra and Norit CA1 were originally steam- and chemically modified activated carbons, respectively, while the others were not modified. Although Norit CA1 was chemically modified, its initial adsorption rate and PSO rate constant were lower than those of Norit SX F Cat, which is an unmodified adsorbent. This can be attributed to its repulsion of organics in solution with a pH of 7.85, as it has a pH_{pzc} of 2.54, leading to a negatively charged surface.[65−67] On the other hand, the lower PSO rate constant and initial rate observed are thought to be related to the very low surface area of AC Puriss compared to other activated carbons.

The sorption of organic matter onto activated carbon is a complicated process, in which the characteristics of both the absorbent and the adsorbate are important. The three sequential steps that can be applied to control the adsorption process are (1) bulk solution transport, (2) film diffusion, and (3) pore diffusion and adsorption, in which the adsorbate is transported to available adsorption sites within the pores of activated carbon. The adsorption process may involve one or more of these stages; the one with the slowest rate determines how much material is absorbed.[68,69] Pore diffusion should exhibit a straight line with a slope equal to k_i (shown in eq 4) if it is the rate-limiting phase in the adsorption process. Pore diffusion plots frequently display many linear segments; therefore, the procedure cannot be that straightforward in practice.[70] These linear segments may reflect pore diffusion in pores with progressively smaller sizes. The IPDM results are given in Figure 5, and the adsorption of organic matter onto activated carbons consisting of basically two steps was attributed to possibly rapid intraparticle diffusion.[62,71,72] As seen from the figure, the plots were nonlinear and did not cross the origin; it may be inferred that the chemical reaction or film diffusion is the limiting step.[69] Further, since the plots of q_t

Table 4. Adsorption Kinetic Model Parameters for NOM Adsorbed on Tested PACs

	pseudo-first-order				pseudo-second-order			
adsorbents	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (1/h)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg-h)	R^2	H
Norit SX Ultra	6.82	2.41	0.20	0.85	6.75	0.39	0.99	17.83
Norit CA1	5.56	1.36	0.005	0.85	5.49	0.24	0.99	7.32
Norit SX F Cat	7.33	10.83	0.02	0.74	7.28	0.25	0.99	13.42
AC Puriss	6.46	1.02	0.13	0.66	6.39	0.19	0.99	7.96

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771

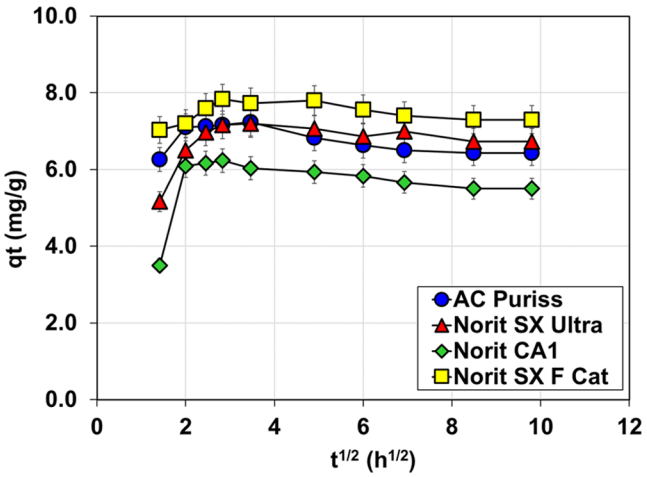


Figure 5. Weber–Morris model for the adsorption kinetics of NOM on the tested carbons.

against $t^{1/2}$ did not yield a straight line, the parameters for the interparticle diffusion model could not be determined.

3.4. Adsorption Equilibrium Models. Two widely used empirical isothermal adsorption models, Langmuir and Freundlich, were applied to fit the equilibrium adsorption data of DOC at different adsorbent doses in order to determine the affinity of equilibrium organic matter adsorption onto selected activated carbons. The Langmuir model assumes that there is a uniform surface having a fixed number of sites, and only one solute molecule is adsorbed per site. On the other hand, the assumptions for the Freundlich isotherm are the occurrence of adsorbate uptake on a heterogeneous surface by multilayer adsorption and the increase of the amount of the adsorbate adsorbed infinitely with the increase in concentration.[73−75] The modified Freundlich isotherm model is used to define the adsorption isotherm of multicomponent and unknown organic mixtures with different adsorption affinities and to better compare the measured adsorption parameters (DOC and UV_{254}) with the predicted ones.[76−78] In this study, dose-base the dose-based normalized modified Freundlich isotherm model was applied to experimental data. The goodness of fit of data to linearized Langmuir and modified Freundlich models was evaluated using eqs 5 and 6, respectively

$$\frac{1}{q_e} = \frac{1}{q_m K_L}\frac{1}{C_e} + \frac{1}{q_m} \tag{5}$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln\frac{C_e}{M} \tag{6}$$

The separation factor was calculated as follows (eq 7).

$$R_L = \frac{1}{1 + K_L C_0} \tag{7}$$

In these equations, q_e and q_m indicate the amounts adsorbed at equilibrium and the maximum adsorption capacity of the adsorbent (mg/g), respectively. K_L and K_F are the adsorption constants at equilibrium for Langmuir and modified Freundlich isotherm models, respectively. $1/n$ denotes the adsorbent surface affinity varying with the heterogeneity of surface site energy distribution. M is the adsorbent dosage. R_L is the separation factor representing the Langmuir isotherm feature, and C_0 is the initial adsorbate concentration.

Isotherm model parameters obtained as a result of linearized analysis of Langmuir ($1/q_e$ vs $1/C_e$) and modified Freundlich ($\log q_e$ vs $\log C_e$/dose) isotherm models are given in Tables 5 and 6, respectively. The modified Freundlich isotherm better fitted the organic matter removal data for all adsorbents than the Langmuir isotherms, with correlation coefficients of 0.98–0.99 (R^2). The weaker fit of the experimental data to the Langmuir isotherm model was observed, as high adsorbate concentrations at equilibrium predicted low adsorption capacity. The Langmuir model is generally not suitable for adsorption in the case of a high concentration of the adsorbate at equilibrium, since the Langmuir isotherm model disrupts the assumptions of single-layer coverage, site equivalence, and site independence.[68]

The dose-based linearized modified Freundlich isotherm for organic matter adsorption from acetochlor- and metolachlor-containing water samples is depicted in Figure 6A,B, respectively. $1/n$, a measure of adsorption density or surface heterogeneity, is the slope of the modified isotherm plot and ranges from 0 to 1; the closer the value to 0, the greater the heterogeneity.[79] The values of $1/n$, obtained from the modified Freundlich isotherm for acetochlor- and metolachlor-containing water samples, vary from 0.70 to 0.76 and from 0.72 to 0.79, respectively, indicating that the adsorption of organic matter by all tested activated carbons was favorable and suggested an irreversible chemisorption process ($1/n < 1$) as reported in the study of adsorption of organic matter by powdered activated carbon by many researchers.[75,80−82]

The characteristic of an isotherm is defined by the separation factor of R_L, which indicates whether an isotherm is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$).[73,75,83] Further, the separation factor of R_L values from the Langmuir isotherm ranging between 0.36 and 0.43 for the acetochlor- and metolachlor-containing water samples also supported the favorable adsorption of organic matter by selected adsorbents.[73,83,84] On the other hand, it can be deduced that the adsorption density is weak, and the surface heterogeneity of activated carbon is a less significant factor,

Table 5. Isotherm Parameters of the Langmuir Model for NOM Adsorption in Water Samples Containing Acetochlor and Metolachlor[a]

	acetochlor				metolachlor			
adsorbents	q_m	K_L	R_L	R^2	q_m	K_L	R_L	R^2
Norit SX Ultra	2.53	0.57	0.36	0.90	2.94	0.59	0.36	0.79
Norit CA1	2.34	0.48	0.41	0.82	2.0	0.44	0.43	0.86
Norit SX F Cat	2.24	0.55	0.39	0.81	2.57	0.56	0.38	0.83
AC Puriss	3.16	0.57	0.36	0.60	3.43	0.68	0.39	0.65

[a]The units of q_m and K_L are mg/g and (L/mg), respectively.

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771

Table 6. Isotherm Parameters of the Modified Freundlich Model for NOM Adsorption in Water Samples Containing Acetochlor and Metolachlor

	acetochlor				metolachlor			
adsorbents	$q_{e,max}$ (mg/g)	K_F[a]	$1/n$	R^2	$q_{e,max}$ (mg/g)	K_F[a]	$1/n$	R^2
Norit SX Ultra	120.6	2.50	0.74	0.99	127.2	2.18	0.79	0.99
Norit CA1	86.7	1.84	0.70	0.98	76.7	1.64	0.72	0.98
Norit SX F Cat	91.1	1.70	0.76	0.98	93.5	1.63	0.79	0.98
AC Puriss	99.5	2.58	0.72	0.98	100.6	1.89	0.79	0.99

[a]The unit of K_F is $(mg/g)/(mg/L)^{1/n}$.

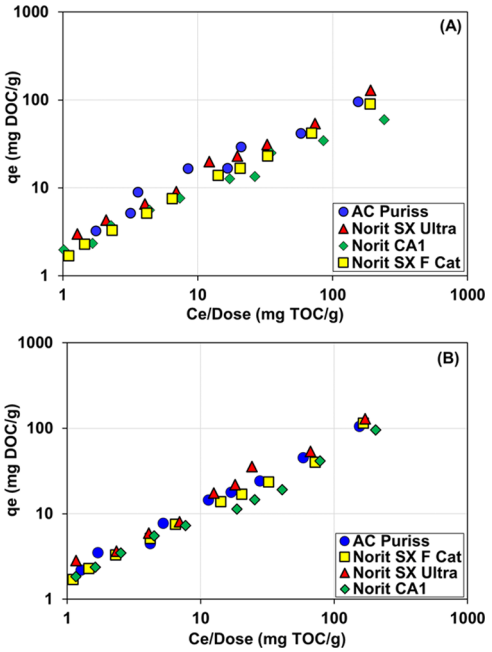


Figure 6. Dose-normalized equilibrium of modified Freundlich isotherm of organic matter by tested activated carbons: (A) Acetochlor-containing samples and (B) metolachlor-containing samples (pH: 7.85, C_0: 2.75 mg/L, T: 25 °C, stirring at 120 rpm).

since the $1/n$ values obtained in experimental studies were close to 1.[65,73,85]

Among the activated carbons, Norit SX Ultra yielded the highest adsorption density with $1/n$ values of 0.74 and 0.79 for the acetochlor and metolachlor samples, respectively. The K_F values range from 1.70 to 2.58 $(mg/g)/(mg/L)^{1/n}$ for the acetochlor samples and from 1.63 to 2.18 $(mg/g)/(mg/L)^{1/n}$ for the metolachlor samples. The highest K_F values of 2.20 and 2.58 $(mg/g)/(mg/L)^{1/n}$ for the acetochlor samples and 2.18 and 1.89 $(mg/g)/(mg/L)^{1/n}$ for the metolachlor samples revealed stronger adsorption of organic matter onto Norit SX Ultra and AC Puriss, respectively. Similar to the highest affinity (K_F) observed between the adsorbent and the adsorbate, the maximum modified Freundlich isotherm capacities of 120.6 and 99.5 mg/g for acetochlor and 127.2 and 100.6 mg/g for metolachlor were obtained by Norit SX Ultra and AC Puriss, respectively. Similarly, Lu and Su[86] determined the Freundlich isotherm parameters of K_F and $1/n$ as 3.86 and 0.63, and Iriarte-Velasco et al.[67] reported them as 5.85 and 0.63 for organic matter removal by activated carbon, respectively. Interestingly, although Norit CA1 was chemically modified and had a higher surface area than Norit SX F Cat and AC Puriss, the lowest affinity values and the lowest capacity were provided by this activated carbon. The main reason for this is attributed to the fact that Norit CA1 is negatively charged with a pH_{pzc} value of 2.53 and repels organic compounds. On the other hand, AC Puriss has the lowest surface area; however, it has the highest number of total basic groups (3.9 meq/g), which plays a significant impact on the adsorption of organic compounds.[87]

3.5. Effect of Adsorbent Dose on the Removal of Acetochlor, Metolachlor, and NOM. The removal performances of tested activated carbons for acetochlor, metolachlor, and NOM were evaluated by varying doses from 10 to 1000 mg/L in completely mixed batch reactors at an initial pH of 7.85, a mixing speed of 120 rpm, and a temperature of 25 °C. The surface water samples contained 500 mg/L either acetochlor or metolachlor and 2.75 mg/L NOM. In Table 7, the removal efficiencies of acetochlor, metolachlor, and NOM were presented. Besides, the removal percentages of UV_{254} absorption and SUVA were determined to evaluate the impact of adsorption on the NOM fraction.

As adsorbent doses increased, the removal rates of NOM and UV_{254} also increased. The maximum NOM removal performances were 76, 66, 60, and 72% for acetochlor-containing samples and 71, 61, 60, and 65% for metolachlor-containing samples by Norit SX Ultra, Norit CA1, Norit SX F Cat, and AC Puriss, respectively. Although Norit CA1 had the lowest equilibrium capacity, it provided higher NOM removal performance than Norit SX F Cat at an adsorbent dose of 1000 mg/L. On the other hand, the highest and lowest UV_{254} removal performances were observed by AC Puriss and Norit CA1 with >99 and 50%, respectively. The fact that SUVA removal rates, especially at higher adsorbent doses, are higher than NOM removal efficiencies by the Norit SX Ultra and AC Puriss carbons indicates that aromatic and hydrophobic organic fractions are selectively removed by these carbons compared to hydrophilic and aliphatic organic substances. The selective removal of aromatic and hydrophobic organic fractions by the Norit SX Ultra and AC Puriss carbons might be attributed to the higher surface area of Norit SX Ultra and the higher total surface basic groups of AC Puriss. It is reported that the adsorption of amino and carboxylic groups on the adsorbent surface binds to the functional −OH group, and the number of total basic groups on the adsorbent surface affects the adsorption of organic compounds. As the amount of total basic groups on the adsorbent surface increases, the adsorption of organic compounds consisting of amino and carboxylic groups can be enhanced.[87]

In general, greater removal performances for acetochlor and metolachlor were obtained by all PACs, and both herbicides could be removed from the aqueous solution between 90 and >98% (Table 7). The highest acetochlor removal was observed by Norit SX Ultra, Norit CA1, and AC Puriss PACs, that is, >98% of acetochlor was adsorbed over 75 mg/L adsorbent dosages. However, an adsorbent dose higher than 500 mg/L should be applied in order to achieve over 98% acetochlor

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771

Table 7. Effect of the Adsorbent Dose on the Removal of Acetochlor, Metolachlor, and NOM (%)[a]

	Norit SX Ultra				Norit CA1				Norit SX F Cat				AC Puriss			
adsorbent dose (mg/L)	AcCl[b]	DOC	UV_{254}	SUVA	AcCl[b]	DOC	UV_{254}	SUVA	AcCl[b]	DOC	UV_{254}	SUVA	AcCl[b]	DOC	UV_{254}	SUVA
10	92	40	5	0	80	20	5	0	86	32	5	0	91	38	41	1
25	94	42	42	6	94	29	9	0	95	38	27	0	95	41	45	3
50	95	49	63	32	98	42	5	0	92	41	36	0	92	58	68	21
75	93	54	79	57	>98	34	9	0	93	45	55	0	95	50	77	53
100	>98	62	84	61	>98	43	14	0	94	49	50	0	>98	66	86	58
200	>98	57	84	66	>98	51	27	0	94	54	77	28	>98	71	91	67
300	>98	62	89	74	>98	56	32	0	94	55	77	27	>98	62	95	88
500	>98	67	95	85	>98	62	36	0	94	59	86	49	>98	65	91	73
750	>98	70	95	84	>98	58	36	0	>98	61	82	32	>98	71	99	99
1000	>98	76	95	82	>98	66	50	0	>98	60	86	45	>98	72	99	99
	Norit SX Ultra				Norit CA1				Norit SX F Cat				AC Puriss			
adsorbent dose (mg/L)	MeCl[c]	DOC	UV_{254}	SUVA	MeCl[c]	DOC	UV_{254}	SUVA	MeCl[c]	DOC	UV_{254}	SUVA	MeCl[c]	DOC	UV_{254}	SUVA
10	>98	43	8	0	90	32	4	0	97	41	8	0	>98	40	58	0
25	>98	45	27	0	91	35	8	0	98	36	12	0	>98	43	73	16
50	>98	60	31	0	97	32	12	0	98	42	23	0	>98	47	85	44
75	>98	55	65	31	>98	36	15	0	>98	45	27	0	>98	51	88	66
100	>98	58	73	42	>98	38	27	0	>98	49	58	20	>98	56	88	72
200	>98	54	88	78	>98	49	38	0	>98	54	88	76	>98	60	92	69
300	>98	59	92	83	>98	55	46	0	>98	55	88	75	>98	52	92	77
500	>98	61	96	91	>98	58	54	0	>98	59	69	28	>98	67	98	81
750	>98	71	96	88	>98	59	56	0	>98	61	81	52	>98	63	98	93
1000	>98	71	96	88	>98	61	35	0	>98	60	85	63	>98	65	99	99

[a]All values represent the removal percentage of related parameters. [b]AcCl: acetochlor. [c]MeCl: metolachlor.

removal with Norit SX F Cat. On the other hand, metolachlor was almost completely removed by Norit SX Ultra and AC Puriss PACs, even at very low adsorbent dosages. Similarly, Norit CA1 and Norit SX F Cat provided higher metolachlor removal performances, and the results showed that it could be reduced to over 98% with higher than 50 mg/L doses.

The results were consistent with the study of Dai et al.,[88] that is, acetochlor and metolachlor were removed successfully with the maximum efficiencies of 91.25 and 73.65% for 10 mg/L coal fly ash, respectively. Similarly, Wang et al.[7] and Wang et al.[89] reported 96.3 and >97.5% adsorption performances by the activated carbon and modified sorbent for acetochlor, respectively. In the metolachlor adsorption study with three different biochar pyrolyzed at different temperatures, removal performances varying between 15 and 91% were obtained depending on the pyrolysis degree of the biochar and the initial metolachlor concentration.[90] Acetochlor and metolachlor are nonionic compounds, and they are characterized as less polar ($3 < \log K_{ow} < 4$) by their $\log K_{ow}$ coefficients of 3.13 and 4.14, respectively (Table 1). The relatively higher adsorption efficiencies of metolachlor at a low adsorbent dose might be attributed to its higher $\log K_{ow}$ value than that of acetochlor, although their octanol−water partition coefficients are similar.

Besides, the nonionic nature of acetochlor and metolachlor caused the repulsion effect between the adsorbent and pollutant to be less significant, even though Norit CA1 is negatively charged at pH 7.85. Indeed, the possible sorption driving forces for nonionic pesticides like acetochlor and metolachlor are hydrogen and $\pi-\pi$ bonds and van der Waals interaction rather than electrostatic interactions; therefore, the pH_{pzc} values of PACs did not have much effect on the adsorption behavior of pesticides.[91,92] Even though they have a wide pH_{pzc} range, all adsorbents provided similar removal efficiencies, i.e., higher than 90% for acetochlor and metolachlor.

Adsorption studies have shown that for adsorbents having heterogeneous micropore size distribution, NOM competes with micropollutants dominantly by the direct site mechanism, and also primarily and the most favorable competition is the direct site for the NOM fraction, whose molecular size is closer to that of micropollutants.[93] The lower SUVA removal observed at low adsorbent doses could possibly be associated with adsorption of low-molecular-weight, hydrophilic, and relatively aliphatic organics. Further, the relatively lower removal efficiencies for acetochlor and metolachlor at low adsorbent doses may be attributed to the readily occupied active adsorption sites of PACs by such organics. The results show that the low-molecular-weight NOM fraction is more competitive with acetochlor. On the other hand, a removal performance of over 98% was achieved even at the lowest dose in metolachlor adsorption by Norit SX Ultra and AC Puriss adsorbents. Similarly, Ling et al.[28] reported that the inhibition of micropollutant adsorption was caused by the direct site competition of low- or medium-molecular-weight organics and/or pore blocking of high-molecular-weight organics. Kennedy and Summers[27] stated that the significant reduction in adsorption capacities of methylisoborneol and warfarin was observed because of increasing direct site competition. On the other hand, Hu et al.[26] observed that the low-molecular-weight hydrophobic NOM fraction was mostly responsible for competition in atrazine and caffeine adsorption. Wang et al.[7] reported that humic acid, a component of NOM, competed with acetochlor for the adsorption sites of activated carbon functionalized with $MnFe_2O_4$, and the competition was more pronounced with the increase of humic acid concentration. Yu et al.[94] stated that the removal of some fraction of NOM by coagulation pretreatment reduces the competition with the

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771

micropollutants against the adsorbent and increases the micropollutant removal efficiency.

4. CONCLUSIONS

In this study, we examined the removal of acetochlor, metolachlor, and NOM from surface waters with the low-SUVA characteristic by four different PACs (Norit SX Ultra, Norit CA1, Norit SX F Cat, and AC Puriss). Besides, the adsorption characteristics of PACs in terms of kinetic and isotherm models were evaluated.

The adsorption kinetic data of organic matter were well described by the PSO model for all tested activated carbons, with the kinetic rate constants changing between 0.19 and 0.39 g/mg-h. The chemical reaction or film diffusion was the rate-limiting step for adsorption. While the isotherm parameters well-obeyed the modified Freundlich isotherm, the highest NOM adsorption capacities were achieved by Norit SX Ultra with 120.6 and 127.2 mg/g and by AC Puriss with 99.5 and 100.6 mg/g for acetochlor- and metolachlor-containing samples, respectively.

Acetochlor and metolachlor were successfully removed with efficiencies in the range of 90−98% by all PACs, especially even at very low adsorbent dosages by Norit SX Ultra and AC Puriss. The possible mechanisms that occurred during adsorption of acetochlor and metolachlor by PACs were chemical and physical sorption, respectively. The adsorption affinity of PACs for acetochlor and metolachlor were in the order of Norit SX Ultra > AC Puriss > Norit CA1 > Norit SX F Cat and Norit SX Ultra > AC Puriss > Norit SX F Cat > Norit CA1, respectively. In general, the competitive effect of NOM on the adsorption of nonionic acetochlor and metolachlor, observed at low adsorbent dosages, indicates that low-molecular-size organic substances compete for the active sites of the adsorbent. Moreover, the inhibitory effect of NOM was more effective for acetochlor at low adsorbent doses for all PACs, while it was only observed for metolachlor in Norit CA. In practical applications, 100−200 mg/L Norit SX Ultra or AC Puriss can be applied for the efficient removal of acetochlor, metolachlor, and NOM at pH values of 7−8 for the treatment of waters like Altinapa surface water with NOM having low-molecular-weight organics and low-SUVA characters.

Future studies should also focus on the competitive effects of low-molecular-weight NOM fractions (e.g., neutral, hydrophilic, or hydrophobic acids and bases) and temperature effects on adsorption of nonionic pesticides by PACs and thorough investigation for nonionic pesticides' physical and chemical interactions with PAC active sites.

AUTHOR INFORMATION

Corresponding Author

Nuray Ates − *Department of Environmental Engineering, Erciyes University, Kayseri 380320, Turkey;* orcid.org/0000-0002-8923-4852; Email: nuraya@erciyes.edu.tr

Authors

Emine Yilmaz − *Graduate School of Natural and Applied Sciences, Erciyes University, Kayseri 380320, Turkey*

Ezgi Altiparmak − *Graduate School of Natural and Applied Sciences, Erciyes University, Kayseri 380320, Turkey*

Filiz Dadaser-Celik − *Department of Environmental Engineering, Erciyes University, Kayseri 380320, Turkey*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.3c02588

Author Contributions

E.Y. and E.A.: experimenting, collecting data, and writing the manuscript. F.D.-C.: designing the work, writing the manuscript, and review and editing. N.A.: designing the work, collecting data, formal analysis, visualization, writing the manuscript, and review and editing. All authors read and approved the final manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank the Scientific and Technological Research Council of Turkey (TUBITAK; Project No. 118Y402) and Erciyes University Research Fund (Project Nos. FYL-2021-11301 and FYL-2021-11304) for the financial support.

REFERENCES

(1) Mojiri, A.; Zhou, J. L.; Robinson, B.; Ohashi, A.; Ozaki, N.; Kindaichi, T.; Farraji, H.; Vakili, M. Pesticides in aquatic environments and their removal by adsorption methods. *Chemosphere* **2020**, *253*, No. 126646.

(2) Tudi, M.; Ruan, H. D.; Wang, L.; Lyu, J.; Sadler, R.; Connell, D.; Chu, C.; Phung, D. T. Agriculture Development, Pesticide Application and Its Impact on the Environment. *Int. J. Environ. Res. Public Health* **2021**, *18*, 1112.

(3) Anderson, T. A.; Salice, C. J.; Erickson, R. A.; McMurry, S. T.; Cox, S. B.; Smith, L. M. Effects of landuse and precipitation on pesticides and water quality in playa lakes of the southern high plains. *Chemosphere* **2013**, *92*, 84−90.

(4) de Souza, R. M.; Seibert, D.; Quesada, H. B.; Bassetti, F. D.; Fagundes-Klen, M. R.; Bergamasco, R. Occurrence, impacts and general aspects of pesticides in surface water: A review. *Process Saf. Environ. Prot.* **2020**, *135*, 22−37.

(5) Bernasinska, J.; Duchnowicz, P.; Koter-Michalak, M.; Koceva-Chyla, A. Effect of safeners on damage of human erythrocytes treated with chloroacetamide herbicides. *Environ. Toxicol. Pharmacol.* **2013**, *36*, 368−377.

(6) Vryzas, Z.; Alexoudis, C.; Vassiliou, G.; Galanis, K.; Papadopoulou-Mourkidou, E. Determination and aquatic risk assessment of pesticide residues in riparian drainage canals in northeastern Greece. *Ecotoxicol. Environ. Saf.* **2011**, *74*, 174−181.

(7) Wang, Y. Q.; Lin, C. Y.; Liu, X. T.; Ren, W. B.; Huang, X. K.; He, M. C.; Ouyang, W. Efficient removal of acetochlor pesticide from water using magnetic activated carbon: Adsorption performance, mechanism, and regeneration exploration. *Sci. Total Environ.* **2021**, *778*, No. 146353.

(8) *Regulatory Determinations Support Document for Selected Contaminants from the Second Drinking Water Contaminant Candidate List (CCL 2)* United States Environmental Protection Agency: Washington, DC; 2008.

(9) Lo, Y. C.; Yang, C. C.; Deng, J. F. Acute alachlor and butachlor herbicide poisoning. *Clin. Toxicol.* **2008**, *46*, 716−721.

(10) Foley, M. E.; Sigler, V.; Gruden, C. L. A multiphasic characterization of the impact of the herbicide acetochlor on freshwater bacterial communities. *ISME J.* **2008**, *2*, 56−66.

(11) Bradley, P. M.; Journey, C. A.; Romanok, K. M.; Barber, L. B.; Buxton, H. T.; Foreman, W. T.; Furlong, E. T.; Glassmeyer, S. T.; Hladik, M. L.; Iwanowicz, L. R.; Jones, D. K.; Kolpin, D. W.; Kuivila, K. M.; Loftin, K. A.; Mills, M. A.; Meyer, M. T.; Orlando, J. L.; Reilly, T. J.; Smalling, K. L.; Villeneuve, D. L. Expanded Target-Chemical Analysis Reveals Extensive Mixed Organic-Contaminant Exposure in US Streams. *Environ. Sci. Technol.* **2017**, *51*, 4792−4802.

(12) *Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Public Law 104. 61 Statutes at Large Chapter 125* United States Environmental Protection Agency: Washington, DC; 1947.

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771

(13) *Final Contaminant Candidate List 3 Chemicals: Classification of the PCCL to CCL* United States Environmental Protection Agency: Washington, DC; 2009.
(14) EU. Directive 2013/39/EC of the European Parliament and of the Council of 12 August 2013 Amending Directives 2000/60/EC and 2008/105/EC as Regards Priority Substances in the Field of Water Policy Text with EEA Relevance. *Off. J. Eur. Union* **2013**, *226*, 1−17.
(15) MFWA. *Surface Water Quality Regulation. Affairs MFWA Official Gazette: 28483*, 2012.
(16) Vagi, M. C.; Petsas, A. S. Recent advances on the removal of priority organochlorine and organophosphorus biorecalcitrant pesticides defined by Directive 2013/39/EU from environmental matrices by using advanced oxidation processes: An overview (2007-2018). *J. Environ. Chem. Eng.* **2020**, *8*, No. 102940.
(17) Luo, Y.; Guo, W. S.; Ngo, H. H.; Nghiem, L. D.; Hai, F. I.; Zhang, J.; Liang, S.; Wang, X. C. C. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Sci. Total Environ.* **2014**, *473*−*474*, 619−641.
(18) Saleh, I. A.; Zouari, N.; Al-Ghouti, M. A. Removal of pesticides from water and wastewater: Chemical, physical and biological treatment approaches. *Environ. Technol. Innovation* **2020**, *19*, No. 101026.
(19) Marican, A.; Duran-Lara, E. F. A review on pesticide removal through different processes. *Environ. Sci. Pollut. Res.* **2018**, *25*, 2051−2064.
(20) Baig, N.; Ihsanullah; Sajid, M.; Saleh, T. A. Graphene-based adsorbents for the removal of toxic organic pollutants: A review. *J. Environ. Manage.* **2019**, *244*, 370−382.
(21) Velusamy, K.; Chellam, P.; Kumar, P. S.; Venkatachalam, J.; Periyasamy, S.; Saravanan, R. Functionalization of MXene-based nanomaterials for the treatment of micropollutants in aquatic system: A review. *Environ. Pollut.* **2022**, *301*, No. 119034.
(22) Saravanan, A.; Kumar, P. S.; Srinivasan, S.; Jeevanantham, S.; Vishnu, M.; Amith, K. V.; Sruthi, R.; Saravanan, R.; Vo, D. V. N. Insights on synthesis and applications of graphene-based materials in wastewater treatment: A review. *Chemosphere* **2022**, *298*, No. 134284.
(23) Yu, C. H.; Betrehem, U. M.; Ali, N.; Khan, A.; Ali, F.; Nawaz, S.; Sajid, M.; Yang, Y.; Chen, T. T.; Bilal, M. Design strategies, surface functionalization, and environmental remediation potentialities of polymer-functionalized nanocomposites. *Chemosphere* **2022**, *306*, No. 135656.
(24) Humbert, H.; Gallard, H.; Suty, H.; Croue, J. P. Natural organic matter (NOM) and pesticides removal using a combination of ion exchange resin and powdered activated carbon (PAC). *Water Res.* **2008**, *42*, 1635−1643.
(25) Li, Q. L.; Snoeyink, V. L.; Marinas, B. J.; Campos, C. Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: the roles of PAC pore size distribution and NOM molecular weight. *Water Res.* **2003**, *37*, 4863−4872.
(26) Hu, J. Y.; Martin, A.; Shang, R.; Siegers, W.; Cornelissen, E.; Heijman, B.; Rietveld, L. Anionic exchange for NOM removal and the effects on micropollutant adsorption competition on activated carbon. *Sep. Purif. Technol.* **2014**, *129*, 25−31.
(27) Kennedy, A. M.; Summers, R. S. Effect of DOM Size on Organic Micropollutant Adsorption by GAC. *Environ. Sci. Technol.* **2015**, *49*, 6617−6624.
(28) Ling, Y.; Alzate-Sanchez, D. M.; Klemes, M. J.; Dichtel, W. R.; Helbling, D. E. Evaluating the effects of water matrix constituents on micropollutant removal by activated carbon and beta-cyclodextrin polymer adsorbents. *Water Res.* **2020**, *173*, No. 115551.
(29) Sang, D.; Cimetiere, N.; Giraudet, S.; Tan, R.; Wolbert, D.; Le Cloirec, P. Adsorption-desorption of organic micropollutants by powdered activated carbon and coagulant in drinking water treatment. *J. Water Process Eng.* **2022**, *49*, No. 103190.
(30) Marsolla, L. D.; Brito, G. M.; Freitas, J. C. C.; Coelho, E. R. C. Removing 2,4-D micropollutant herbicide using powdered activated carbons: the influence of different aqueous systems on adsorption process. *J. Environ. Sci. Health, Part B* **2022**, *57*, 588−596.
(31) Archer, A. D.; Singer, P. C. An evaluation of the relationship between SUVA and NOM coagulation using the ICR database. *J. Am. Water Works Assoc.* **2006**, *98*, 110−123.
(32) Edzwald, J. K.; Tobiason, J. E. Enhanced coagulation: US requirements and a broader view. *Water Sci Technol.* **1999**, *40*, 63−70.
(33) Weishaar, J. L.; Aiken, G. R.; Bergamaschi, B. A.; Fram, M. S.; Fujii, R.; Mopper, K. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **2003**, *37*, 4702−4708.
(34) Ates, N.; Kitis, M.; Yetis, U. Formation of chlorination by-products. in waters with low SUVA-correlations with SUVA and differential UV spectroscopy. *Water Res.* **2007**, *41*, 4139−4148.
(35) Hua, G. H.; Reckhow, D. A.; Abusallout, I. Correlation between SUVA and DBP formation during chlorination and chloramination of NOM fractions from different sources. *Chemosphere* **2015**, *130*, 82−89.
(36) Otero, R.; Lopez, M. I.; Esquivel, D.; Fernandez, J. M.; Romero-Salguero, F. J. Removal of S-metolachlor herbicide from aqueous solutions by meso and microporous organosilica materials. *Microporous Mesoporous Mater.* **2019**, *278*, 35−43.
(37) Otero, R.; Esquivel, D.; Ulibarri, M. A.; Romero-Salguero, F. J.; Van Der Voort, P.; Fernandez, J. M. Mesoporous phenolic resin and mesoporous carbon for the removal of S-Metolachlor and Bentazon herbicides. *Chem. Eng. J.* **2014**, *251*, 92−101.
(38) Gomis-Berenguer, A.; Sidoli, P.; Cagnon, B. Adsorption of Metolachlor and Its Transformation Products, ESA and OXA, on Activated Carbons. *Appl. Sci.* **2021**, *11*, 7342.
(39) Gomis-Berenguer, A.; Laidin, I.; Renoncial, S.; Cagnon, B. Study of enantioselective metolachlor adsorption by activated carbons. *RSC Adv.* **2020**, *10*, 40321−40328.
(40) Ilavský, J.; Barloková, D.; Marton, M. In *Removal of Selected Pesticides from Water Using Granular Activated Carbon*, Paper Presented at the IOP Conference Series: Earth and Environmental Science, Czech Republic, 25−26 November, 2021.
(41) Ates, N.; Dadaser-Celik, F.; Kaplan-Bekaroglu, S. S. In *Pesticides Pollution from Agriculture Activities in the Altinapa Reservoir Watershed, Turkey*, XIII International Agriculture Symposium "AGROSYM 2022", Sarajevo, Bosna-Hersek, 2022; pp 1−6.
(42) National Library of Medicine, National Center for Biotechnology Information. Summary Compounds. https://pubchem.ncbi.nlm.nih.gov/compound/4169 (accessed September 28, 2022).
(43) Weber, W. J.; Morris, J. C. Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div.* **1963**, *89*, 31−59.
(44) *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; APHA/AWWA/WEF: Washington, DC, 2012.
(45) Dastgheib, S. A.; Karanfil, T.; Cheng, W. Tailoring activated carbons for enhanced removal of natural organic matter from natural waters. *Carbon* **2004**, *42*, 547−557.
(46) Foo, K. Y.; Hameed, B. H. Detoxification of pesticide waste via activated carbon adsorption process. *J. Hazard. Mater.* **2010**, *175*, 1−11.
(47) Salman, J. M.; Njoku, V. O.; Hameed, B. H. Adsorption of pesticides from aqueous solution onto banana stalk activated carbon. *Chem. Eng. J.* **2011**, *174*, 41−48.
(48) Shokry, H.; Elkady, M.; Hamad, H. Nano activated carbon from industrial mine coal as adsorbents for removal of dye from simulated textile wastewater: operational parameters and mechanism study. *J. Mater. Res. Technol.* **2019**, *8*, 4477−4488.
(49) ShamsiJazeyi, H.; Kaghazchi, T. Investigation of nitric acid treatment of activated carbon for enhanced aqueous mercury removal. *J. Ind. Eng. Chem.* **2010**, *16*, 852−858.
(50) Njoku, V. O.; Islam, M. A.; Asif, M.; Hameed, B. H. Adsorption of 2,4-dichlorophenoxyacetic acid by mesoporous activated carbon prepared from H3PO4-activated langsat empty fruit bunch. *J. Environ. Manage.* **2015**, *154*, 138−144.
(51) Gao, Q.; Chen, F. H.; Zhang, J. L.; Hong, G. Y.; Ni, J. Z.; Wei, X.; Wang, D. J. The study of novel Fe3O4@gamma-Fe2O3 core/shell

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771

nanomaterials with improved properties. *J. Magn. Magn. Mater.* **2009**, *321*, 1052−1057.
(52) Silva, C. F.; Menezes, L. F.; Pereira, A. C.; Nascimento, C. S. Molecularly Imprinted Polymer (MIP) for thiamethoxam: A theoretical and experimental study. *J. Mol. Struct.* **2021**, *1231*, No. 129980.
(53) Mohammad, S. G.; Ahmed, S. M. Preparation of environmentally friendly activated carbon for removal of pesticide from aqueous media. *Int. J. Ind. Chem.* **2017**, *8*, 121−132.
(54) Ebrahimzadeh, S.; Wols, B.; Azzellino, A.; Kramer, F.; van der Hoek, J. P. Removal of organic micropollutants in a drinking water treatment plant by powdered activated carbon followed by rapid sand filtration. *J. Water Process Eng.* **2022**, *47*, No. 102792.
(55) Dastgheib, S. A.; Rockstraw, D. A. A model for the adsorption of single metal ion solutes in aqueous solution onto activated carbon produced from pecan shells. *Carbon* **2002**, *40*, 1843−1851.
(56) Guillossou, R.; Le Roux, J.; Mailler, R.; Pereira-Derome, C. S.; Varrault, G.; Bressy, A.; Vulliet, E.; Morlay, C.; Nauleau, F.; Rocher, V.; Gasperi, J. Influence of dissolved organic matter on the removal of 12 organic micropollutants from wastewater effluent by powdered activated carbon adsorption. *Water Res.* **2020**, *172*, No. 115487.
(57) Zhang, S. J.; Shao, T.; Karanfil, T. The effects of dissolved natural organic matter on the adsorption of synthetic organic chemicals by activated carbons and carbon nanotubes. *Water Res.* **2011**, *45*, 1378−1386.
(58) Liu, F. F.; Fan, J. L.; Wang, S. G.; Ma, G. H. Adsorption of natural organic matter analogues by multi-walled carbon nanotubes: Comparison with powdered activated carbon. *Chem. Eng. J.* **2013**, *219*, 450−458.
(59) Velten, S.; Knappe, D. R. U.; Traber, J.; Kaiser, H. P.; von Gunten, U.; Boller, M.; Meylan, S. Characterization of natural organic matter adsorption in granular activated carbon adsorbers. *Water Res.* **2011**, *45*, 3951−3959.
(60) Ho, Y. S.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* **1999**, *34*, 451−465.
(61) Yu, J.; Lv, L.; Lan, P.; Zhang, S. J.; Pan, B. C.; Zhang, W. M. Effect of effluent organic matter on the adsorption of perfluorinated compounds onto activated carbon. *J. Hazard. Mater.* **2012**, *225*−*226*, 99−106.
(62) Ersan, G.; Kaya, Y.; Ersan, M. S.; Apul, O. G.; Karanfil, T. Adsorption kinetics and aggregation for three classes of carbonaceous adsorbents in the presence of natural organic matter. *Chemosphere* **2019**, *229*, 515−524.
(63) Ittisupornrat, S.; Phihusut, D.; Kitkaew, D.; Sangkarak, S.; Phetrak, A. Performance of dissolved organic matter removal from membrane bioreactor effluent by magnetic powdered activated carbon. *J. Environ. Manage.* **2019**, *248*, No. 109314.
(64) Yang, H. Y.; Zheng, X.; Zhang, D.; Tang, G.; Li, X. L.; Wu, H.; Yan, W.; Zhi, H. G. Comparison of the effect of PANI/TiO2, Dow resins and activated carbon in removing model dissolved organic matter (DOM) and phosphorus. *J. Water Process Eng.* **2021**, *43*, No. 102302.
(65) Cho, E. J.; Kang, J. K.; Moon, J. K.; Um, B. H.; Lee, C. G.; Jeong, S.; Park, S. J. Removal of triclosan from aqueous solution via adsorption by kenaf-derived biochar: Its adsorption mechanism study via spectroscopic and experimental approaches. *J. Environ. Chem. Eng.* **2021**, *9*, No. 106343.
(66) Fairey, J. L.; Speitel, G. E.; Katz, L. E. Impact of natural organic matter on monochloramine reduction by granular activated carbon: The role of porosity and electrostatic surface properties. *Environ. Sci. Technol.* **2006**, *40*, 4268−4273.
(67) Iriarte-Velasco, U.; Alvarez-Uriarte, J. I.; Chimeno-Alanis, N.; Gonzalez-Velasco, J. R. Natural Organic Matter Adsorption onto Granular Activated Carbons: Implications in the Molecular Weight and Disinfection Byproducts Formation. *Ind. Eng. Chem. Res.* **2008**, *47*, 7868−7876.
(68) Singh, S. K.; Townsend, T. G.; Mazyck, D.; Boyer, T. H. Equilibrium and intra-particle diffusion of stabilized landfill leachate onto micro- and meso-porous activated carbon. *Water Res.* **2012**, *46*, 491−499.
(69) Viegas, R. M. C.; Campinas, M.; Costa, H.; Rosa, M. J. How do the HSDM and Boyd's model compare for estimating intraparticle diffusion coefficients in adsorption processes. *Adsorption* **2014**, *20*, 737−746.
(70) Malash, G. F.; El-Khaiary, M. I. Piecewise linear regression: A statistical method for the analysis of experimental adsorption data by the intraparticle-diffusion models. *Chem. Eng. J.* **2010**, *163*, 256−263.
(71) Zhang, S. J.; Shao, T.; Kose, H. S.; Karanfil, T. Adsorption of Aromatic Compounds by Carbonaceous Adsorbents: A Comparative Study on Granular Activated Carbon, Activated Carbon Fiber, and Carbon Nanotubes. *Environ. Sci. Technol.* **2010**, *44*, 6377−6383.
(72) Wu, F. C.; Tseng, R. L.; Juang, R. S. Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics. *Chem. Eng. J.* **2009**, *153*, 1−8.
(73) Zhao, Z. M.; Sun, W. J.; Ray, M. B. Adsorption isotherms and kinetics for the removal of algal organic matter by granular activated carbon. *Sci. Total Environ.* **2022**, *806*, No. 150885.
(74) Ahn, S. K.; Park, K. Y.; Song, W. J.; Park, Y. M.; Kweon, J. H. Adsorption mechanisms on perfluorooctanoic acid by FeCl3 modified granular activated carbon in aqueous solutions. *Chemosphere* **2022**, *303*, No. 134965.
(75) Al-Ghouti, M. A.; Da'ana, D. A. Guidelines for the use and interpretation of adsorption isotherm models: A review. *J. Hazard. Mater.* **2020**, *393*, No. 122383.
(76) Gui, H. J.; Li, F. S.; Wei, Y. F.; Yamada, T. Adsorption characteristics of natural organic matter on activated carbons with different pore size distribution. *Int. J. Environ. Sci. Technol.* **2018**, *15*, 1619−1628.
(77) Li, F. S.; Yuasa, A.; Ebie, K.; Azuma, Y.; Hagishita, T.; Matsui, Y. Factors affecting the adsorption capacity of dissolved organic matter onto activated carbon: modified isotherm analysis. *Water Res.* **2002**, *36*, 4592−4604.
(78) Summers, R. S.; Roberts, P. V. Activated Carbon Adsorption of Humic Substances. 1. Heterodisperse Mixtures and Desorption. *J. Colloid Interface Sci.* **1988**, *122*, 367−381.
(79) Tan, I. A. W.; Ahmad, A. L.; Hameed, B. H. Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies. *J. Hazard. Mater.* **2008**, *154*, 337−346.
(80) Bhavsar, K. S.; Labhane, P. K.; Huse, V. R.; Dhake, R. B.; Sonawane, G. H. Activated carbon immobilized WO3 nanocuboids: Adsorption/photocatalysis synergy for the enhanced removal of organic pollutants. *Inorg. Chem. Commun.* **2020**, *121*, No. 108215.
(81) Vergili, I.; Gencdal, S. Removal of Organic Matter and Etodolac from Pharmaceutical Industry Wastewater by PAC Adsorption. *Water Environ. Res.* **2017**, *89*, 641−651.
(82) Amosa, M. K.; Jami, M. S.; Alkhatib, M. F. R.; Jimat, D. N.; Muyibi, S. A. A Two-Step Optimization and Statistical Analysis of COD Reduction from Biotreated POME Using Empty Fruit Bunch-Based Activated Carbon Produced from Pyrolysis. *Water Qual. Exposure Health* **2015**, *7*, 603−616.
(83) Nethaji, S.; Sivasamy, A.; Mandal, A. B. Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglans regia shell biomass. *Int. J. Environ. Sci. Technol.* **2013**, *10*, 231−242.
(84) Reddy, P. M. K.; Mahammadunnisa, S.; Ramaraju, B.; Sreedhar, B.; Subrahmanyam, C. Low-cost adsorbents from bio-waste for the removal of dyes from aqueous solution. *Environ. Sci. Pollut. Res.* **2013**, *20*, 4111−4124.
(85) Jaichuedee, J.; Sinyoung, S.; Suttinun, O.; Musikavong, C. Characterization of ultra-micropore powder activated carbon for use in removing regulated disinfection by-product precursors. *J. Water Process Eng.* **2022**, *49*, No. 103049.
(86) Lu, C. Y.; Su, F. S. Adsorption of natural organic matter by carbon nanotubes. *Sep. Purif. Technol.* **2007**, *58*, 113−121.

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771

(87) Chen, K.-C.; Wang, Y. H. The effects of Fe-Mn oxide and TiO2/alpha-Al2O3 on the formation of disinfection by-products in catalytic ozonation. *Chem. Eng. J.* **2014**, *253*, 84−92.
(88) Dai, Y. J.; Pan, Z. L.; Xing, C. M.; Chen, X.; Bai, J. N.; Bai, Z. Z.; Jin, L. Y.; Zhang, N. X.; Jiang, H. T.; Tang, J. A.; Gao, Y. W.; Shan, D. X. Rapid adsorption of acetochlor and metolachlor from aqueous solution onto solid waste coal fly ash. *Desalin. Water Treat.* **2020**, *205*, 222−235.
(89) Wang, B.; Yang, Y.; Lu, Y.; Wang, W.; Wang, Q. W.; Dong, X. W.; Zhao, J. H. Rapid and efficient removal of acetochlor from environmental water using Cr-MIL-101 sorbent modified with 3, 5-Bis(trifluoromethyl) phenyl isocyanate. *Sci. Total Environ.* **2020**, *710*, No. 135512.
(90) Wei, L.; Huang, Y. F.; Huang, L. X.; Li, Y. L.; Huang, Q.; Xu, G. Z.; Muller, K.; Wang, H. L.; Ok, Y. S.; Liu, Z. Z. The ratio of H/C is a useful parameter to predict adsorption of the herbicide metolachlor to biochars. *Environ. Res.* **2020**, *184*, No. 109324.
(91) Mondol, M. M. H.; Jhung, S. H. Adsorptive removal of pesticides from water with metal-organic framework-based materials. *Chem. Eng. J.* **2021**, *421*, No. 129688.
(92) Ighalo, J. O.; Adeniyi, A. G.; Adelodun, A. A. Recent advances on the adsorption of herbicides and pesticides from polluted waters: Performance evaluation via physical attributes. *J. Ind. Eng. Chem.* **2021**, *93*, 117−137.
(93) Pelekani, C.; Snoeyink, V. L. Competitive adsorption in natural water: Role of activated carbon pore size. *Water Res.* **1999**, *33*, 1209−1219.
(94) Yu, Z. R.; Peldszus, S.; Huck, P. M. Adsorption characteristics of selected pharmaceuticals and an endocrine disrupting compound - Naproxen, carbamazepine and nonylphenol - on activated carbon. *Water Res.* **2008**, *42*, 2873−2882.

https://doi.org/10.1021/acsomega.3c02588
ACS Omega 2023, 8, 31758−31771