REMOVAL OF ACETOCHLOR AND METOLACHLOR BY ADSORPTION PROCESS

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

Department of Environmental Engineering, Erciyes University, Kayseri, 38280, Turkey

*nuraya@erciyes.edutr

Abstract

Purpose: The aim of this study was to investigate the removal performances of acetochlor and metolachlor by four different activated carbons.

Methods: The kinetic rates and isotherm models were determined for AC Puriss, Norit SX F Cat, Norit SX Ultra, and Norit CA1 adsorbents. Kinetic tests were conducted during 2-96 hours at a constant 300 mg/L adsorbent dose. Isotherm tests were performed for different adsorbent dosages from 10 mg/L to 1000 mg/L. Acetochlor and metolachlor were analyzed by a HPLC instrument performing the DLLME method. Extracted acetochlor and metolachlor samples were analyzed at 210 and 230 nm wavelengths, respectively.

Results: Time for reaching the equilibrium state and adsorption capacity were evaluated based on kinetic and isotherm results. The adsorption rate for all adsorbents followed pseudo-second-order kinetic model. The isotherm test results were best fitted to the modified Freundlich isotherm. The highest adsorption capacity was observed with the AC Puriss activated carbon and the lowest adsorption capacity was obtained with the Norit CA1 adsorbent for water samples containing acetochlor and metolachlor. While acetochlor removal performances of AC Puriss and Norit CA1 was >95, metolachlor was removed completely with the AC Puriss and Norit SX Ultra adsorbents even in very low adsorbent dosages.

Conclusion: Among the tested adsorbents, AC Puriss provided the highest adsorption capacity of 102.5 and 106.7 mg/g for acetochlor and metolachlor containing samples, respectively. Moreover, acetochlor and metolachlor were completely removed with AC Puriss for all adsorbent dosages. In general, acetochlor and metolachlor could be removed by 99% for 10-100 mg/L adsorbent dosages.

Keywords: Acetochlor, metolachlor, adsorption, isotherm, capacity.

Introduction

Pesticides are complex compounds or mixtures of compounds used for agriculture, forestry, industry and domestic purposes to eliminate unwanted pests and weeds and increase agricultural yield [1-3]. The most used pesticides are herbicides (53%) followed by fungicides (22%) and insecticides (17%) [4, 5]. Pesticide concentration in surface waters is related to crop and soil management practices in the basin [6]. Runoff is the main diffuse source of pesticides reaching surface waters and is dependent on pesticide application and physicochemical properties and watershed variables. Basin variables include the slope of the pesticide applied area, crop type, organic carbon content, size of the area, vegetation type, and the density of the buffer zones between agricultural areas and water bodies [7]. Many health problems and disorders have been associated with pesticide residues and their metabolites [4]. Also, pesticides have been considered significantly toxic due to their ability to bioaccumulate in organism tissues and migrate to higher organisms [1]. Conventional water and wastewater treatment processes are not specifically designed for pesticide removal; therefore advanced treatment processes are required. Various treatment processes can be used for removal of pesticides such as biological oxidation, advanced oxidation, photocatalytic degradation, membrane filtration, ozonation, ion exchange and adsorption [8]. Among these processes, adsorption is a promising method since it is more efficient and cost-effective in addition to its simplicity and flexibility of design, ease of operation and insensitivity to toxic contaminants. However, the major drawback of adsorption is the requirement of regeneration after it becomes fully loaded by contaminants [9]. The adsorption efficiency of pesticides depends on the properties of pesticides (molecular weight, polarity, hydrophobicity, ionic nature, functional groups, water solubility etc.) and adsorbent (number of sites available, porosity, surface area, structure, surface chemistry, type, surface groups and size), the physicochemical characteristics of solution (pH, temperature, ionic strength etc.) [9, 10]. In this study, we examine removal of acetochlor and metolachlor, two widely used pesticides, by the adsorption process.

Materials and Methods

In the experimental studies, 500 µg/L of acetochlor and metolachlor were spiked in surface water samples with total organic carbon (TOC) value of 2.55 mg/L (ave) collected from Altinapa Reservoir (Turkey). In adsorption experiments, four different activated carbons (AC Puriss, Norit SX F Cat, Norit SX Ultra, and Norit CA1) were used. Adsorption tests were carried out following two sequential phases: (1) kinetic tests and (2) equilibrium tests to determine the time to reach equilibrium and their adsorption capacities. Kinetic tests were performed in 125 ml (sample volume of 100 mL) polytetrafluoroethylene amber glass bottles at a fixed adsorbent dose of 300 mg/L. The samples were shaken horizontally at 120 rpm on the shaker for 2, 4, 8, 12, 24, 36, 48, 72 and 96 hours to determine the equilibrium time. In the equilibrium experiments, ten different resin doses between 10 and 1000 mg/L were added to the samples, then shaken horizontally at 120 rpm at room temperature (20 ± 5°C). The pH of all samples

was adjusted to be between 8±0.1 with H_2SO_4 or NaOH. At the end of contact period, the samples were filtered using 0.45 µm filter paper and stored in fridge until further analysis. Acetochlor, metolachlor, TOC, pH and UV absorbance analysis were performed in the samples collected from kinetic and isotherm tests. TOC values were subjected to adsorption rate and capacity determination.

Acetochlor and metolachlor were analysed by dispersive liquid-liquid micro extraction method using the HPLC instrument. A total of eight calibration standards were prepared using the standard mixture of acetochlor and metolachlor. For calibration and sample analysis, 400 µL 1,2-dichloroethane and 1 mL acetonitrile solvent mixtures, and 300 µL 1,2-dichloroethane and 1 mL methanol solvent mixtures were added into 8 ml of acetochlor and metolachlor samples, respectively. First, the samples were mixed for 1 min at vortex mixer, then the samples were centrifuged for 2.0 min at 6000 rpm to separate organic phases from aqueous phase. A 100 µL organic phase was taken into an insert vial for analysis by HPLC instrument. Acetochlor and metolachlor were analysed at 210 and 230 nm wavelengths, respectively.

Results and Discussion

The sorption capacity (adsorbed TOC by adsorbents) was determined by the mass balance equation provided in Equation 1.

$$q_e = \frac{(C_o - C_e)V}{M} \quad \text{(Eq. 1)}$$

In Equation (1), C_o and C_e are the initial and equilibrium TOC concentrations in the aqueous phase (mg/L), respectively; q is the equilibrium adsorption capacity (mg/g); V is the sample volume (L); and M is the dry weight of the adsorbent (g).

Kinetic parameters were explicated by applying the pseudo-first-order and pseudo-second-order kinetic models to predict the rate of TOC adsorption by tested activated carbons. The first- and second-order kinetic models were linearized as in Equations 2 and 3.

$$Ln(q_e - q_t) = Ln(q_{e)} - k_1 t \quad \text{(Eq. 2)}$$

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

In these equations, k_1 (L/h) and k_2 (g/mg.h) are the rate constants of pseudo-first and second-order sorption, and q_t and q_e are the sorption capacities (mg/g) at time t and at equilibrium, respectively.

The results showed that the adsorption of organic matter by the activated carbons was consistent with pseudo-second order model. Furthermore, the calculated equilibrium capacity

($q_{e,calc}$) by the pseudo-second-order kinetic model represents experimental equilibrium capacity ($q_{e,exp}$) better compared to the pseudo-first-order kinetic model.

The isotherm test results were best fitted to the modified Freundlich isotherm which represents the relation between equilibrium capacity and resin dose normalized aqueous phase concentration. In the modified Freundlich Equation (Equation 4), K_F is the Freundlich capacity parameter for heterogeneous systems and n is the coefficient showing the distribution of the energy sites on the adsorbent and the magnitude of the adsorption repulsive forces:

$$q_e = K_F \left(\frac{C_e}{M}\right)^{1/n} \quad \text{(Eq. 4)}$$

The dose-normalized q_e, K_F, n, R^2 and values obtained from isotherm tests for acetochlor and metolachlor are shown in Table 1. The highest adsorption capacity was observed by AC Puriss activated carbon (102.5 and 106.7 mg/g), the lowest adsorption capacity was obtained by Norit CA1 adsorbent (52.7 and 50.3 mg/g) for water samples containing acetochlor and metolachlor.

Table 1. Modified Freundlich isotherm parameters for TOC adsorption by adsorbents.

	Acetochlor				Metolachlor			
Adsorbent Type	$q_{e,exp}$ (mg/g)	K_F	n	R^2	$q_{e,exp}$ (mg/g)	K_F	n	R^2
Norit SX F Cat	85.6	2.62	1.50	0.98	84.3	1.36	1.31	0.99
AC Puriss	102.5	2.68	1.37	0.98	106.7	1.91	1.27	0.99
Norit SX Ultra	69.2	1.89	1.48	0.99	95.2	1.82	1.30	0.98
Norit CA1	52.7	1.45	1.63	0.95	50.3	1.28	1.56	0.97

The pesticides removal performances were calculated based on pesticides concentrations at time zero and t (Equation 5):

$$\%\ Removal = \frac{(C_0 - C_t)}{C_0} * 100 \quad \text{(Eq. 5)}$$

Acetochlor and metolachlor removal performances of four activated carbons were given in Figure 1 and Figure 2. The acetochlor removal performances of AC Puriss and Norit CA1 were >95 even in low adsorbent concentrations (Figure 1). The removal performances of Norit SX Fcat were between 85-99% for adsorbent dose from 10 mg/L to 1000 mg/L. Similarly, Norit SX Ultra removed acetochlor with 91-99% efficiency. As shown Figure 2, metolachlor was removed completely by AC Puriss and Norit SX Ultra even in very low adsorbent dosages. Metolachlor removal performance was increased from 90% to complete removal by adsorbent

dosages from 10 mg/L to 75 mg/L. On the other hand, 10-300 mg/L of Norit CA1 dosages provided 96-99% removal efficiencies for metolachlor.

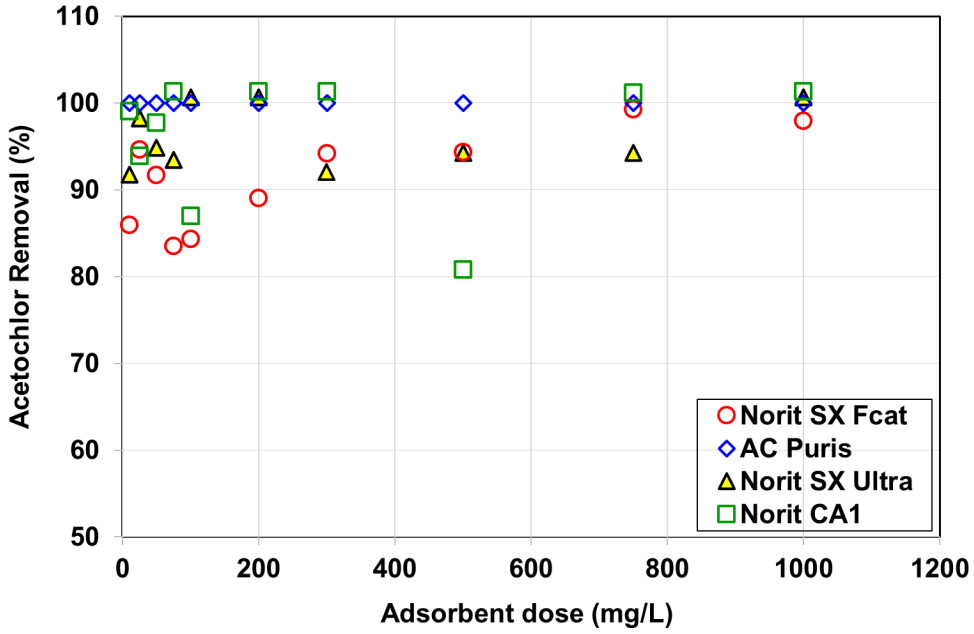

Figure 1. Removal performances of tested activated carbons for Acetochlor

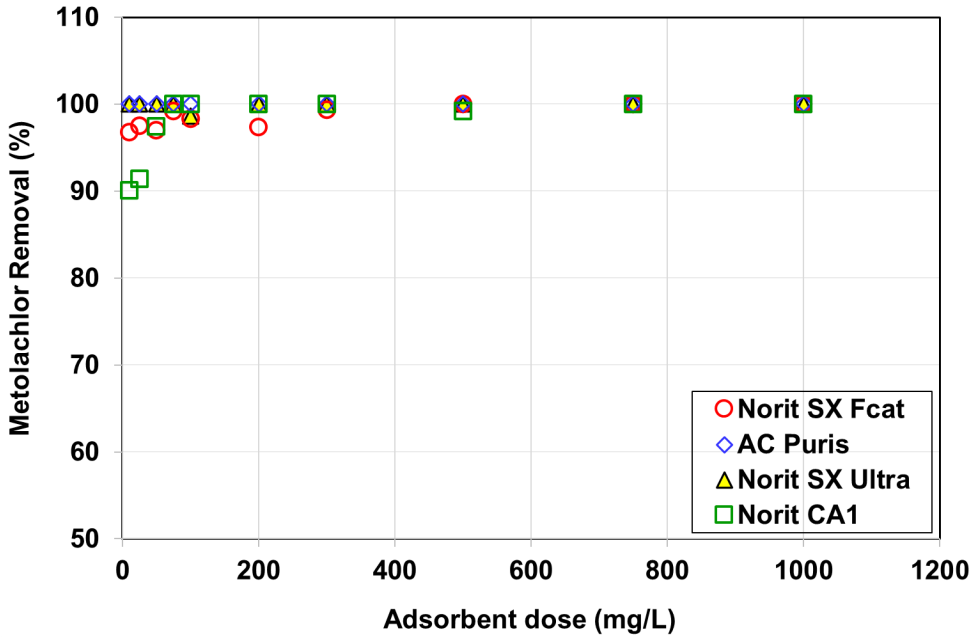

Figure 2. Removal performances of tested activated carbons for Metolachlor

Acknowledgments

This study was financially supported by the Scientific and Technological Research Council of Turkey-TUBITAK (Project No. 118Y402) and Erciyes University Research Fund (Project No. FYL-2021-11301 and FYL-2021-11304).

References

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

[2] Kafaei, R., Arfaeinia, H., Savari, A., Mahmoodi, M., Rezaei, M., Rayani, M., Sorial, G.A., Fattahi, N. and Ramavandi, B.: Organochlorine pesticides contamination in agricultural soils of southern Iran. Chemosphere. 240 (2020)

[3] Li, Z.J. and Jennings, A.: Worldwide Regulations of Standard Values of Pesticides for Human Health Risk Control: A Review. Int J Env Res Pub He. 14 (7) (2017)

[4] Sharma, A., Shukla, A., Attri, K., Kumar, M., Kumar, P., Suttee, A., Singh, G., Barnwal, R.P. and Singla, N.: Global trends in pesticides: A looming threat and viable alternatives. Ecotox Environ Safe. 201 (2020)

[5] FAO: Pesticides use, pesticides trade and pesticides indicators 1990-2019, Food and Agriculture Organization of the United Nations (2021)

[6] Anderson, T.A., Salice, C.J., Erickson, R.A., McMurry, S.T., Cox, S.B. and Smith, L.M.: Effects of landuse and precipitation on pesticides and water quality in playa lakes of the southern high plains. Chemosphere. 92 (1), 84-90 (2013)

[7] Cole, J.T., Baird, J.H., Basta, N.T., Huhnke, R.L., Storm, D.E., Johnson, G.V., Payton, M.E., Smolen, M.D., Martin, D.L. and Cole, J.C.: Influence of buffers on pesticide and nutrient runoff from bermudagrass turf. J Environ Qual. 26 (6), 1589-1598 (1997)

[8] Ahmad, T., Rafatullah, M., Ghazali, A., Sulaiman, O., Hashim, R. and Ahmad, A.: Removal of Pesticides from Water and Wastewater by Different Adsorbents: A Review. J Environ Sci Heal C. 28 (4), 231-271 (2010)

[9] Saleh, I.A., Zouari, N. and Al-Ghouti, M.A.: Removal of pesticides from water and wastewater: Chemical, physical and biological treatment approaches. Environ Technol Inno. 19 (2020)

[10] Mojiri, A., Zhou, J.L., Robinson, B., Ohashi, A., Ozaki, N., Kindaichi, T., Farraji, H. and Vakili, M.: Pesticides in aquatic environments and their removal by adsorption methods. Chemosphere. 253 (2020)