ZSM-5 AS SORBENT FOR REMOVAL OF LINURON FROM WATER

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ABSTRACT

Zeolite Socony Mobil-5 (ZSM-5) was used as sorbent to remove linuron pesticide from water. The main parameters of adsorption process such as dosages of adsorbent, contact time and initial concentration of linuron were investigated. Removal efficiencies ranged from 89.50 % to 69.91 % as the initial linuron concentration increased from 2 to 15 mg L^{-1}. Results were modelled by adsorption isotherms: Langmuir, Freundlich and Temkin isotherms. The best correlation was achieved with Temkin adsorption isotherm. Adsorption kinetics of linuron has been studied by the pseudo-first-order model and the pseudo-second-order model. The kinetic studies showed significant correlation for the pseudo- second -order model which indicates that linuron is chemisorbed on analysed zeolite.

Key words: pesticide, water treatment, zeolite, adsorption, separation.

INTRODUCTION

Pesticides as protection agents for plant diseases have an essential role to improve agricultural activities and increase food production. The wide application of pesticides also causes environmental problems related to the distribution of pesticides in the environment, particularly to water ecosystems [1]. Pesticides are often detected at low concentration levels and commonly occur in the form of complex mixtures, which are harmful to life because of their toxicity, carcinogenicity and mutagenicity [2,3]. This is the reason for development efficient remediation techniques to remove pesticides from the water environment [4].

Natural zeolites have a strong ability to adsorb water molecules without the crystal structure of zeolites. The polarity, shape and size of the diffusing molecules present one of the essential characteristics to choose the adsorption relative to the geometry of pores of the zeolites. Zeolite Socony Mobil-5 (ZSM-5) is an aluminosilicate with the chemical formula of $Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O$ (0<n<27). Zeolite ZSM-5 has a very high temperature and acid stability (>1000 °C and down to pH=3, respectively). It is synthesized at high temperatures and pressures in an autoclave coated with Teflon and is characterized by low water solubility. Zeolite ZSM-5 is a type of a "high-silica"-Zeolite, which is responsible for most of its special properties.

The aim of this paper is to investigate the influence of main parameters such as pH, contact time, mass of adsorbent ZSM-5 and initial concentration of selected pesticide on the removal of linuron from aquatic media. Linuron (3-(3, 4-dichlorophenyl)-1-methoxy-1-methylurea) belongs to the group of herbicides which are widely applied for elimination of weeds bean, wheat, corn, sugarcane and potato.

EXPERIMENTAL

Measurements were conducted at the room temperature (25 ± 2 °C). Zeolite ZSM-5 (manufacturer Acros Organics, Geel, Belgium) was used as adsorbent for removal of linuron. Total surface area (BET) of ZSM-5 is 390 m^2g^{-1}. The batch experiments were carried out by varying pH, concentrations of linuron, contact time and amount of adsorbent. The mixtures were shaken at 140 rpm at room temperature. The analyses of linuron removal were performed using HPLC-DAD (1260, Agilent Infinity). Separation was performed with a reversed phase column Eclipse XDB-C18 (3 x 150 mm, particle size 3.5µm). The operating conditions were:

the flow of 0.8 mL min^{-1}, the temperature of the column was 25 ºC and injection volume of 10 µL. The isocratic separation with the ratio of mobile phases of 50:50 (water and acetonitrile) was used.

Adsorbed amount, q_e (mg g^{-1}), was calculated via the equation:

$$q_e = \frac{(C_0 - C_f)}{m} * V \qquad (1)$$

where q_e is the adsorption capacity (mg g^{-1}), C_0 and C_f are the initial and final linuron concentrations, respectively (expressed in mg L^{-1}), V is the solution volume (mL) and m is the adsorbent dosage (g).

The adsorption isotherms models Langmuir, Freundlich and Temkin were applied for the fitting of the experimental data. The kinetic of the adsorption data was analysed using the pseudo-first order and pseudo-second-order model.

RESULTS AND DISCUSSION

The influence of pH value on the removal of linuron by ZSM-5 was studied for values 3,5,6,7,8 and 10. The recoveries varied from 77.2 % to 87.75 % (from pH 10 to pH of 3). It was observed that the optimum pH value is 3 with removal efficiency of 87.75 %. The optimum mass for removal of linuron was 40.00 g L^{-1} at pH 3.00 and contact time of 60 min. The obtained results indicate that the removal percentage of selected pesticide raises with an increment in the adsorbent dosage from 20.00 to 60.00 g L^{-1} for linuron. With increased adsorbent dosage, the available sorption surface and availability of more adsorption sites rise, which results in more adsorbate attributed to the surfaces.

Table 1. Isotherm constants of the Langmuir, Freundlich and Temkin models for removal of linuron by ZSM-5.

	Isotherm model	Parameters
Langmuir	q_{max} (mg g^{-1})	0.880
	K_L (L mg^{-1})	0.125
	r	0.421
	RMSE	0.020
	χ^2	0.072
Freundlich	K_f	0.111
	1/n	0.804
	r	0.909
	RMSE	0.021
	χ^2	0.037
Temkin	*B* (J L^{-1})	0.108
	A	3.404
	r	0.948
	RMSE	0.024
	χ^2	0.036

Influence of initial concentration on separation of linuron from water was studied at optimal experimental conditions pH = 3.00, adsorbent dose 40.00 g L^{-1}, contact time 60 min and temperature 25.0 ± 1 ˚C, respectively. Removal efficiencies ranged from 89.50 % to 69.91 % as the initial linuron concentration increased from 2 to 15 mg L^{-1}. The adsorption capacity values increased continuously with the increase of initial linuron concentration from 0.038 to 0.30 mg L^{-1}. The results were fitted with Langmuir, Freundlich and Temkin models. Isotherm's best fit was chosen based on the largest correlation coefficient (r) value. The results in Table 1. showed that Temkin isotherm fitted better than the other two isotherms.

The removal of linuron as a function of contact time was observed. The removal increased rapidly as the contact time increased from 5.00 to 120 min. The adsorption process took 60 min to reach equilibrium. Hence, the contact time of 60 min was considered as optimum. The initial concentration of linuron in the solution is significant parameter as the pesticides concentration changes over a broad range in industrial effluents. The kinetic of the adsorption data was analysed using the pseudo-first order and pseudo-second-order model (Figure 1 and Figure 2). These results indicate that the pseudo-second order model portrays more properly the sorption kinetic than the pseudo-first order model. According to literature, the pseudo–second-order kinetic model indicates that adsorption mechanism is based on chemical sorption which involves valency forces through sharing or exchanging electrons between a sorbent and sorbate [5,6].

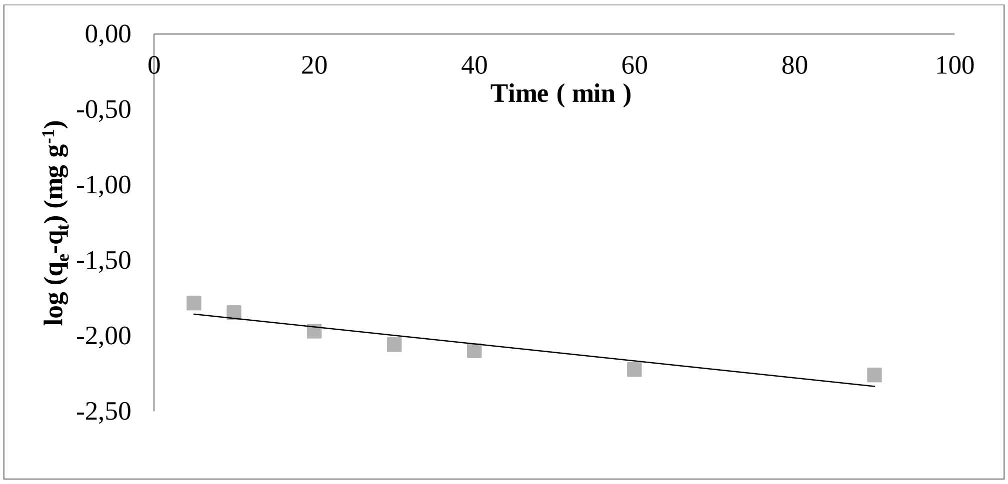

Figure 1. Pseudo-first order kinetics plot of linuron on ZSM-5.

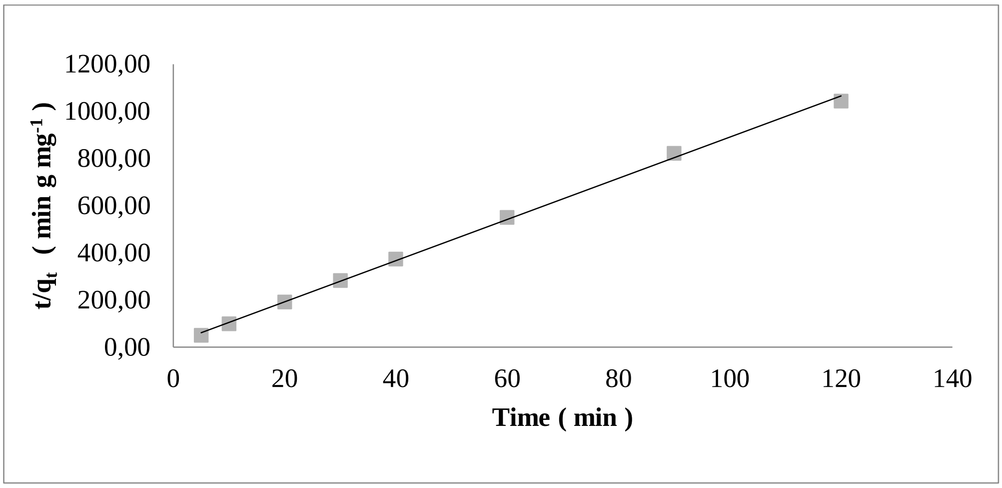

Figure 2. Pseudo-second order kinetics plot of linuron onto ZSM-5.

CONCLUSION

In the current research study, the ZSM-5 zeolite was used as sorbent for separation of linuron from water. The main process parameters such as pH, initial concentration of pesticide, mass of sorbent and contact time were investigated. The equilibrium studies proved that Temkin isotherm model the best describes the adsorption of linuron on zeolite. The kinetic modelling studies showed that kinetics of linuron on zeolite ZSM-5 followed the model of pseudo - second order. The results showed high recovery rates and indicate efficient separation of linuron from water by zeolite ZSM-5.

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REFERENCES

[1] F.W. Shaarani and B.H. Hameed, *Desalination*, 2010, **255 (1)**, 159-164.

[2] R.J. Gilliom, *Environ. Sci. Technol.* 2007, **41 (10)**, 3408-3414.

[3] C. Zhang, Q. Wang, J. Chen, L. Huang, X. Qiao, X. Li and X. Cai, *Environ. Pollut.* 2011, **159 (2)**, 609-615.

[4] L.H. Mendoza-Huizar, *J. Chem.* 2015, **3**, 1-11.

[5] T.R. Sahoo, B. Prelo, Chapter 7 "*Adsorption processes for the removal of contaminants from wastewater: the perspective role of nanomaterials and nanotechnology*" in: "*Nanomaterials for the Detection and Removal of Wastewater Pollutants*", B. Bonelli, F. Freyria, I. Rossetti and R. Sethi (Eds.), Elsevier Science, Amsterdam, 2020, 162-222.

[6] L. Fu, J. Li, G. Wang, Y. Luan and W. Dai, *Ecotoxicol. Environ. Saf.* 2021, **217**, 112207.