ADSORPTION KINETICS AND MECHANISM ANALYSIS OF CYAN PRINTING DYE ON POLYETHYLENE MICROPLASTICS

Vesna Gvoić[1], Maja Lončarski[2], Aleksandra Tubić[2], Sanja Vasiljević[2], Dejan Krčmar[2], Jasmina Agbaba[2], Miljana Prica[1]

[1]Department of Graphic Engineering and Design, Faculty of Technical Sciences, University of Novi Sad, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia
[2]Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia
e-mail: kecic@uns.ac.rs

Abstract

Printing on polymer materials might result with generation of coloured wastewater, enriched with a certain amount of microplastics in a form of polyethylene or polypropylene. In that way, microplastics may acquire the function of carriers of synthetic dyes, heavy metals and other polluting substances. In this paper, kinetics and adsorption mechanism of printing Cyan dye on polyethylene (powdered and granulated), as one of the most common types of microplastics, were investigated. The experiments were performed in a batch mode, in laboratory conditions. Based on the obtained results, a similar adsorption rate degree of selected printing dye was determined on granulated (adsorbed amount was 48.04 μg/g) and powdered material (adsorbed amount was 44.32 μg/g). The adsorption data were fitted well by pseudo-second-order kinetics, while isotherm studies were evaluated using two models: Langmuir and Freundlich. Freundlich and Langmuir equations showed similar performances to fit the solid/liquid distribution of Cyan dye on powdered polyethylene (R^2 = 0.987), whereas Langmuir equation showed slightly better performances for granulated polyethylene than Freundlich equation.

Introduction

Plastic size particles less than 5 mm in diameter, defined as microplastic particles (MPs), are becoming an emerging pollutants due to their ubiquitous interaction with the biotic and abiotic environment. Furthermore, MPs are often added to industrial products, such as dyes, which may be released into the environment after use [1]. The existence of MPs in water bodies has become a concern of researchers in recent years due to their strong sorption capacity for many contaminants: antibiotics [2], polychlorinated biphenyls [3], polycyclic aromatic hydrocarbons [4], heavy metals [5], organochlorine pesticides [6], steroid estrogens [7], etc. Thus, MPs may influence the fate, transport and bioavailability of contaminants in the environment, threatening the ecosystem health. However, little effort has been made to address the adsorptive role of MPs for dyes and the associated underlying interaction mechanisms.

Cyan dye belongs to the group of phthalocyanine dyes, which are characterized by chromophore in a form of four isoindole units linked by nitrogen atoms. It is a derivative of tetrabenzotetraazoporphyrin, complexed with copper metal ion. Due to its high molecular weight and complex structure, phthalocyanine dye is difficult to mineralize. Even discharged into the water bodies with a relatively low concentration, it will be harmful to aquatic organisms [8].

The objectives of this study were to determine adsorption equilibrium and kinetic parameters of Cyan dye on two type of MP particles (powdered (PEp) and granulated (PEg) polyethylene), and to clarify the possible interaction mechanisms between Cyan dye and MPs.

Experimental

Materials. Commercially available MPs in a form of granulated polyethylene (Sigma-Aldrich) and powdered polyethylene (Thermo Fisher Scientific) were used as sorbents. Experiments were performed with Cyan water-based printing dye (C.I.: PB15:3, CAS number: 147-14-8, chemical formula: $C_{32}H_{16}CuN_8$, molar mass: 576.07 g/mol) manufactured by Flint group. The stock solution of Cyan dye was prepared by dissolving 1 g of dye in 1 L of deionized water. The desired concentration of working solution was prepared by diluting stock solution in deionized water.

Adsorption experiments.

Adsorption kinetic experiments of Cyan dye on PEg and PEp particles were conducted in a batch mode, in laboratory conditions. The effect of reaction time on adsorption behavior was conducted in 30 mL solutions with an initial dye concentration of 100 mg/L by adding 30 mg/L of MPs (PEg and PEp). Dye concentration after adsorption experiments were analyzed on UV/VIS spectrophotometer (Genesys 10S, Thermo Fisher) at time intervals of 10 min, 30 min, 1, 2, 3, 4, 5, 6, 24, 36, 48, 72, 96, 144, 192, 264 and 312 h. In order to determine the relationship between adsorption time and adsorption capacity, as well as to analyze the adsorption mechanism of dye on MPs particles, three kinetic models were applied: pseudo-first order, pseudo-second order and Weber-Morris model [1, 9].

Adsorption mechanism of Cyan dye on MPs was evaluated based on the adsorption isotherms, by using seven different initial dye concentrations (1, 5, 25, 50, 100, 150 and 200 µg/L), at a constant sorbent mass of 30 mg. After constant stirring of 72 h, the samples were filtered through a cellulose acetate membrane filter with a porosity of 0.45 µm, and residual dye concentration was determined on a UV/VIS spectrophotometer. The obtained results were analyzed using Freundlich and Langmuir adsorption isotherm models [1].

Results and discussion

Figure 1 shows the adsorption of dye by MPs with increasing reaction time during 312 h. The adsorption of Cyan dye on PEg increased rapidly in first 24 h, then the rate of adsorption slowed down, and equilibrium was reached at 48 h. However, equilibrium between Cyan dye and PEp is established after 72 h.

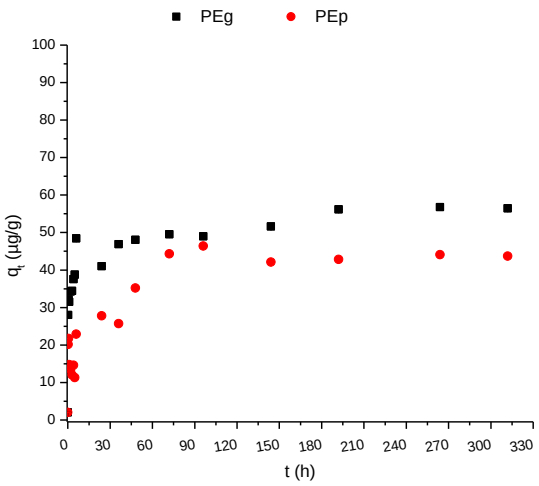

Figure 1. Effects of reaction time on the Cyan adsorption on PEg and PEp

The obtained results indicate that Cyan dye achieved a similar adsorption affinity for both type of MPs, since the adsorbed amount of Cyan on PEg and PEp at equilibrium state were 48.04 µg/g and 44.32 µg/g, respectively. Therefore, the adsorption efficiency is mostly influenced by the type of MPs, while particle size is not crucial.

Three kinetic models were used to describe the adsorption rate and mechanism during adsorption processes of Cyan dye on PEg and PEp: pseudo-first order, pseudo-second order and Weber-Morris model. As shown in Figure 2 and Table 1, the adsorption kinetics were better fitted by pseudo-second-order model (R^2 = 0.958 - 0.999) than pseudo-first-order model (R^2 = 0.332 - 0.606). This indicates that chemisorption was the leading force for the adsorption of dyes on MPs, as well as the adsorption process involves the interaction affinity between sorbents and sorbates [10].

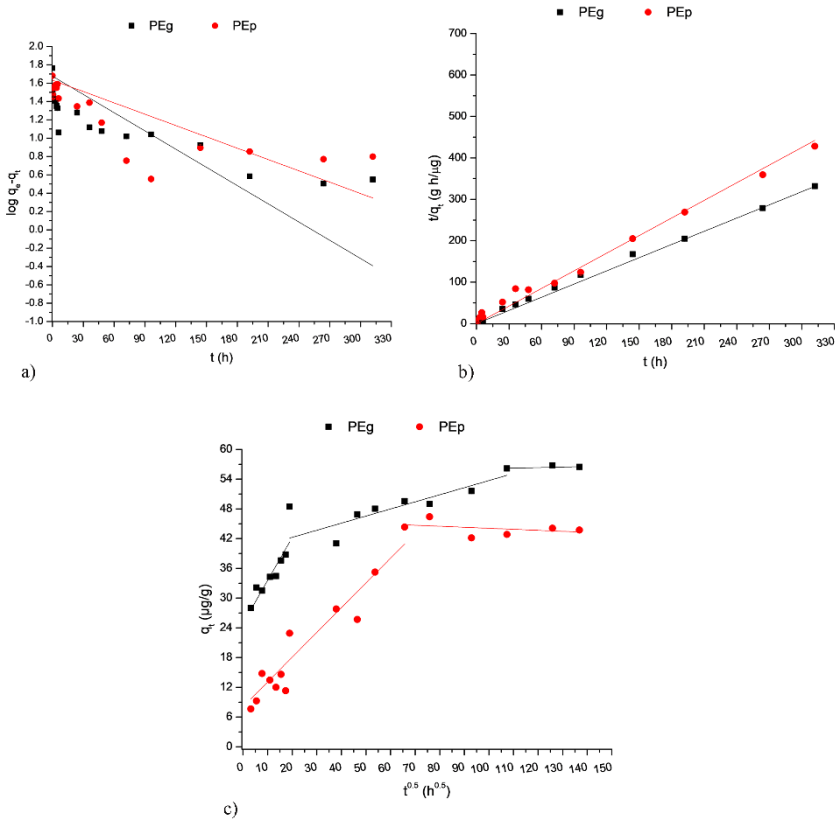

Figure 2. Adsorption kinetic models: (a) pseudo-first-order, (b) pseudo-second-order, (c) Weber-Morris

Table 1. Pseudo-first-order and pseudo-second order kinetic model related parameters

MPs	**Pseudo-first order**			**Pseudo-second order**			
	[a]k_1 (1/h)	[b]q_e (µg/g)	[c]R^2	[d]k_2 (g/µg h)	R^2	[e]q_e (theor.)	q_e (exper.)
PEg	0.00663	5.380	0.332	0.185	0.999	43.200	44.100
PEp	0.00412	5.100	0.606	0.248	0.958	57.100	56.500

[a]k_1 - rate constant of first-order sorption; [b]q_e - adsorption capacity; [c]R^2 - correlation coefficient; [d]k_2 - rate constant of second-order sorption; [e]q_e - equilibrium adsorption coefficient

In order to confirm the validity of the pseudo-second order kinetic model, the experimentally obtained values of the equilibrium adsorption coefficient (q_e experimentally) were compared with theoretical (q_e theoretical) values. Based on the results shown in Table 1, a good agreement is observed, which confirms the fact that Cyan dye adsorption is conducted with chemisorption mechanism on selected types of MPs [11].

In order to explain the complicated adsorption mechanism, including intraparticle diffusion and liquid film diffusion, Weber-Morris kinetic model was used for supplementary interpretation. Based on the results of Weber-Morris kinetic model (Table 2 and Figure 2c) it was determined

that the correlation curves do not pass through the coordinate origin, suggesting that the rate-limiting process was not completely controlled, but probably affected by intraparticle diffusion [12].

Table 2. Weber-Morris kinetic model related parameters

MPs	**[a]K_i (µg/g $h^{1/2}$)**	**[b]C_i (µg/g)**	**R^2**
PEg	0.500	8.086	0.884
	0.020	46.130	0.035
PEp	0.870	24.910	0.850
	0.110	39.400	0.711
	0.090	55.070	0.108

[a]K_i - intraparticle diffusion rate constant;
[b]C_i - thickness liquid film constant

The two-stage and three-stage linear plots in Figure 2c reveal the importance of external mass transfer between the solid and liquid phase, which is explained by the sorbate movement through the aqueous matrix towards the MPs particles, their gradual adsorption on sorbent particles and the establishment of equilibrium state [9]. In that way, adsorption/desorption dynamic equilibrium processes are established for the adsorption of Cyan dye on PEg and PEp particles.

The Langmuir and Freundlich adsorption isotherm models were used to describe the interaction behavior between sorbents and sorbates within the equilibrium states (Figure 3 and Table 3).

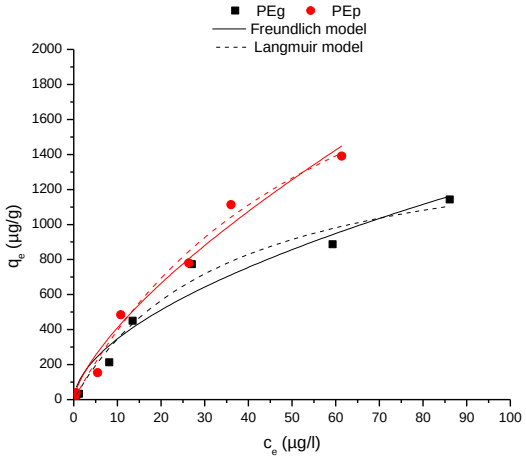

Figure 3. Adsorption isotherms of Cyan dye on PEg and PEp

Table 3. Adsorption isotherms model and related parameters

MPs	**Freundlich model**			**Langmuir model**		
	[a]K_F $(µg/g)/(µg/l)^n$	[b]n	[c]R^2	[d]K_L (l/µg)	[e]q_{max} (µg/g)	R^2
PEg	95.2	0.56	0.947	0.03	1535.9	0.973
PEp	82.7	0.70	0.987	0.02	2874.4	0.987

[a]K_f - Freundlich equilibrium constant; [b]n - adsorption capacity; [c]R^2 - correlation coefficient;
[d]K_L - Langmuir equilibrium constant; [e]q_{max} - maximum adsorption capacity

The Langmuir model achieved a better linear fit for PEg (R^2 = 0.973), indicating that the adsorption occurs on the adsorbent surface with uniform distribution of binding sites. Moreover, the *n* value in Freundlich model is less than 1 for both sorbents, which indicates that the adsorption is chemical process. Furthermore, it was established that adsorption affinity

decreases with covering of available active sites on the MPs surface. Certainly, most adsorption studies preferred to use both of the above isotherm models for data fitting [13].

Conclusion

The present study investigates the adsorption behavior and mechanism of Cyan printing dye on granulated and powdered polyethylene. The adsorption process of dye on microplastics followed the Langmuir isotherm model and the pseudo-second-order kinetics, indicating that monolayer adsorption is mainly controlled by chemical process. Furthermore, Weber-Morris model pointed out to multi-stage adsorption process, revealing that intraparticle diffusion is a limiting factor for the adsorption process. Based on the obtained results, a role of microplastics as a carrier for selected printing dye, if they are released uncontrolled into the environment, is confirmed. Further investigations regarding release of various types of microplastic and printing dyes under different environmental conditions, their interaction and water treatment should be considered.

Acknowledgements

This research has been supported by the Provincial Secretariat for Science and Technological Development, Autonomous Province of Vojvodina through the project: “Synthetic dye removal in the presence of microplastics in advanced water treatment” (Grant No. 142-451-3186/2020-03).

References

[1] H. Li, F. Wang, J. Li, S. Deng, S. Zhang, Chemosphere 264 (2021) 128556.
[2] F. Yu, C. Yang, G. Huang, T. Zhou, Y. Zhao, J. Ma, Sci. Total. Environ. 721 (2020) 137729.
[3] M. A. Fraser, L. Chen, M. Ashar, W. Huang, J. Zeng, C. Zhang, D. Zhang, Ecotox. Environ. Safe. 196 (2020) 110536.
[4] L. Mai, L-J. Bao, L. Shi, L-Y. Liu, E. Y. Zeng, Environ. Pollut. 241 (2018) 834-840.
[5] X. Guo, J. Wang, J. Hazard. Mater. 402 (2021) 123709.
[6] F. Wang, J. Gao, W. Zhai, D. Liu, Z. Zhou, P. Wang, J. Hazard. Mater. 394 (2020) 122517.
[7] B. Hu, Y. Li, L. Jiang, X. Chen, L. Wang, S. An, F. Zhang, J. Hazard. Mater. 400 (2020) 123325.
[8] V. Gvoić, M. Prica, Đ. Kerkez, M. Bečelić-Tomin, A. Kulić Mandić, A. Leovac Maćerak, B. Dalmacija, Acta Periodica Technologica 50 (2019) 77-85.
[9] S. Azizian, J. Colloid. Interface. Sci. 276 (2004) 47-52.
[10] G. Liu, Z. Zhu, Y. Yang, Y. Sun, F. Yu, J. Ma, Environ. Pollut. 246 (2019) 26-33.
[11] Z-Z. Bao, Z-F. Chen, Y. Zhong, G. Wang, Z. Qi, Z. Cai, Sci. Total. Environ. In Press. doi: 10.1016/j.scitotenv.2020.142889.
[12] W. Wang, J. Wang, Chemosphere 193 (2018) 567-573.
[13] T. Huffer, T. Hofmann, Environ. Pollut. 214 (2016) 194-201.