

COMPARATIVE STUDIES CONCERNING THE BEHAVIOUR OF ORGANIC POLLUTANTS IN IASI AREA SOIL

Camelia SMARANDA¹, Laura Carmen APOSTOL¹, Madalina PETRARU¹,
Florentina Anca CALIMAN¹, Maria GAVRILESCU¹

¹ “Gheorghe Asachi” Technical University of Iași

Abstract

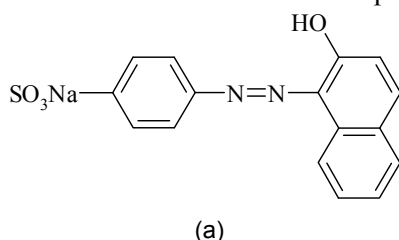
Widespread contamination of soil and groundwater by synthetic organic chemicals (e.g., dyes) has been recognized as an issue of growing importance in recent years. For this reason, is very important to elucidate the fate and transport pathways of these compounds in environmental components. The behavior and persistence of dyes depend on their sorption, transformation, transport and degradation in environmental compartments.

The objectives of the present investigation has been to compare the sorption behaviour of two organic pollutants Acid Orange 7 (C.I. 15510, 350.32 g mol⁻¹) and Erythrosine B (C.I. 45430, M=879.86 g mol⁻¹) onto soil from Iasi area (Romania). The studies were performed by batch mode, at 20⁰ C and natural pH of solution. The adsorption characteristics and dye uptake in soil have been determined by investigating the influence of some parameters (contact time, adsorbent dose and initial dye concentration). It was found that equilibrium sorption amount increases with the increase in initial dye concentration and contact time. Langmuir, Freundlich and Temkin isotherm models were applied to evaluate the adsorption process. Over the entire range of concentration the obtained results show that the adsorption of the studied dyes follows the Freundlich model.

Key words: Acid Orange 7, Erythrosine B, sorption, isotherm

Sorption is the key factors that affect the fate of pollutants in the soil. Many contaminants of ecological interest are very strongly sorbed to soil constituents, so that water-borne advective-dispersive transport through soil is extremely slow for such compounds that include persistent organic pollutants, trace metals and radionuclides (Jarvis et al., 2010). Remediation of soil or ground water is become an important issues in most part of the disposed sites (Mohamed, 2009). Only a few investigations are focused on the behaviour and transport pathway of dye on soil.

The object of this study was to examine the adsorption capacities of two different classes of dyes by soil and the mechanism of their uptake.



MATERIAL AND METHOD

Dyes

Two dyes provided by Sigma Aldrich, Acid Orange 7 (C₁₆H₁₁O₄N₂SNa; C.I. 15510; M=350.32 g mol⁻¹) and Erythrosine B (C₂₀H₆I₄Na₂O₅; C.I. 45430; M=879.86 g mol⁻¹) were used to assess typical experimental behaviour during the batch adsorption studies. Their chemical structures are illustrated in (fig. 1).

The chemical was used in this study as received, without further purification.

Dye was accurately weighed and than dissolved in a proper deionized water volume to prepare the stock solution of 1000 mg L⁻¹. For the experimental assays, dilution of the stock was done to achieve the desired concentration.

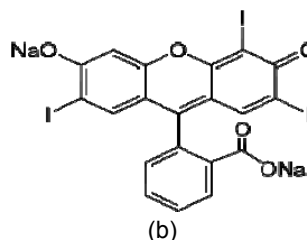


Figure 1 Molecular structure of Acid Orange 7 (a) and Erythrosine B (b)

Soil. The soil samples were collected from the region of Iasi (Romania) from the depth 0-25 cm. The soils were classified as protisol associated with molic gleic/pelic upon Romanian

System of Soil Taxonomy (SRTS-2003). The collected soil was silty clay loam with a composition of 47 % clay minerals, 11 % silica and a content of organic matter of 7.19 %.

The textural properties of the soil were determined by the N₂-BET method using a surface area and porosimetry analyzer (Quantachrome). The surface area, pore volume, average pore diameter external surface area of the soil are 2.626 m² g⁻¹, 4.805 cm³ g⁻¹, 7.317 Å, 1.925 m² g⁻¹ and respectively.

Methods. The sorption experiments were carried out in batch mode. For equilibrium studies fifty milliliters of Acid Orange 7 and Erythrosine B solution with known initial concentration, ranging from 10 to 200 mg L⁻¹ were added to an accurately weighted mass of soil and agitated in a thermostatic shaker (IKA KS 4000 IC Control, Germany) at 150 rpm and 20°C.

The experiments were carried out for 24 hours to ensure that equilibrium was obtained. At the end of the sorption time, the dye solution was separated from the sorbent by centrifugation at 6000 rpm for 20 minutes (Hettich EBA 20 Centrifuge, Germany). The supernatant was filtered through 0.45 μm filter (OlimPeak, Teknokroma) and the dye concentration in the residual solution was analyzed spectrophotometrically at maximum wavelength (CamSpec M 501, UK).

The effect of sorbent dosage was studied with different sorbent doses ranging from 1 to 150 g L⁻¹, using two different initial concentrations 20 mg L⁻¹ of dye. All the experiments were done in duplicate.

The amount of dye adsorbed on soil (q in mg/g) and the percent of pollutants uptake (P) were calculated using the relationships (1, 2):

$$P\% = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

$$q = \frac{(C_i - C_e)V}{m} \quad (2)$$

where, C_i and C_e are the initial and equilibrium concentrations of dye (mgL⁻¹), V is the volume of the dye solution (L) and m is the mass of adsorbent (g).

RESULTS AND DISCUSSIONS

Effect of sorbent dose

The amount of the sorbent is one of the strongly parameters that affect the sorption capacity of the dyes onto soil. The amount of studied dyes sorbed per unit mass of soil decreases with increase in sorbent dose from 1 to 150 g L⁻¹ (fig. 2). This is the result of the fact that a fixed mass of soil is capable to sorb only a certain amount of dye and, the higher amount of soil in the system, the large volume of dye solution that fixed mass of sorbent is able to uptake.

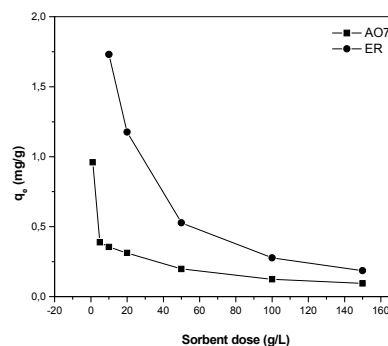


Figure 2 Effect of sorbent dose

Effect of contact time and initial dyes concentration

The amount of dye sorbed per unit of soil mass (mg g⁻¹) improves with contact time increasing and reached the equilibrium after 240 minutes. A large quantity of dye has been sorbed onto soil after a relatively short contact time, where the uptake of more than 50% of the molecules was noticed within the first 60 minutes of the experiments (fig. 3). The rate of removal and sorption capacity are higher in the beginning due to a larger number of vacant surface sites are available for the sorption of the Acid Orange 7 and Erythrosine B during the initial stage. After that, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between dye adsorbed on the soil surface and solution phase.

The two stage sorption mechanism with the first rapid slope and quantitatively significant efficiency has been observed (Smaranda et al., 2009).

Sorption equilibrium isotherms

Equilibrium studies that give the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation. These two isotherms and the Temkin isotherm model were used to assess the different isotherms and their ability to correlate experimental data.

The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The linearized Langmuir equation was used to analyze the data. The equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (3)$$

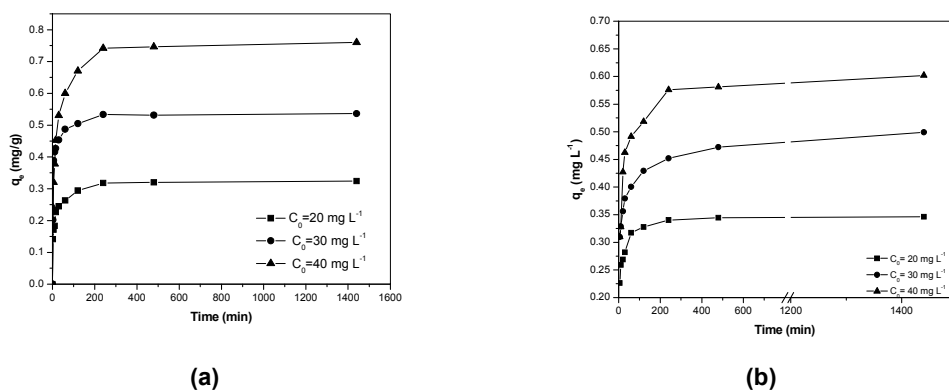


Figure 3 Effect of initial concentration of Acid Orange 7 (a) and Erythrosine B (b) on sorption onto soil

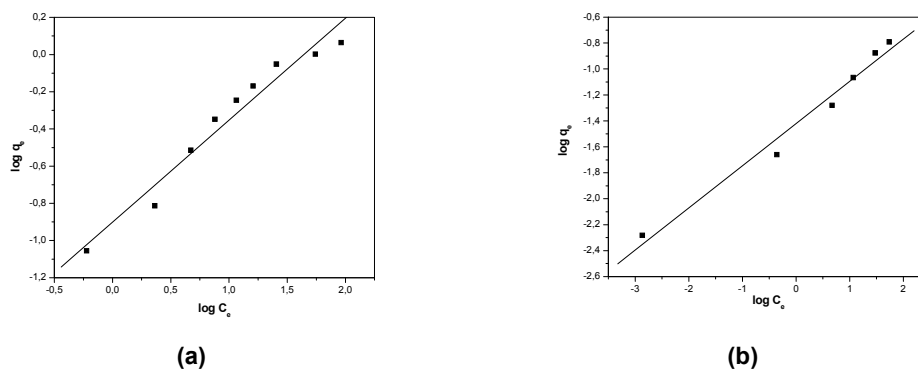


Figure 4 Freundlich isotherm of Acid Orange 7 (a) and Erythrosine B (b) sorption onto soil

where Q_m is the sorbent binding capacity (mg g^{-1}), that is the maximum sorption upon complete saturation of adsorbent surface, K_L the Langmuir adsorption constant, (L mg^{-1}) that is, related to the adsorption/desorption energy. It is well known that the Langmuir equation is intended for a homogeneous surface.

The experimental data were fitted into Eq. 3 for linearization by plotting C_e/Q_e against C_e . The Langmuir constants and coefficient of regression (R^2) are shown on Table 1. The coefficients of regression (R^2) are very poor for the Langmuir isotherm.

The essential feature of the Langmuir isotherm can be expressed by means of ' R_L ', a dimensionless constant referred to as separation factor or equilibrium parameter. The values of R_L indicate the shape of isotherms to be either favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The R_L values obtained in our study indicated that dyes sorption process was favourable (tab 1).

The Freundlich isotherm model was chosen to estimate the adsorption intensity of the sorbent towards the adsorbent. It is an empirical equation employed to describe the isotherm data given by:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where, K_F and n are the Freundlich empirical constants. The linearized form of the Freundlich equation was used for analysis and it is given as:

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

where, C_e is the equilibrium liquid phase concentration (mg L^{-1}) and q_e is solid phase sorbates concentration in equilibrium (mg g^{-1}).

Application of the Freundlich isotherm equation to analyze the equilibrium isotherms of the AO7 and EB gave linear plots (fig. 4). The linear regression coefficient (R^2) and specific parameters are presented on Table 1. The regression coefficient (R^2) ranges from 0.9606 for AO7 to 0.9891 for BR. Generally, this model gave very good fit to the experimental data.

The Freundlich equation frequently gives an adequate description of adsorption data over a restricted range of concentration, even though it is not based on the theoretical background. Apart from homogeneous surface, the Freundlich equation is also suitable for a highly heterogeneous surface and an adsorption isotherm lacking a plateau, indicating a multilayer adsorption (Wong et al., 2008). The values of n is higher than 1, indicating a favourable sorption process. Therefore, the K_F values which are higher for the EB confirms that the adsorption capacity of the soil for this pollutants was greater than AO7.

Table 1

The experimental and predicted isotherm parameters

Isotherm model	Isotherm parameter	Acid orange 7	Erythrosine B
Langmuir	q_e (exp) (mg g ⁻¹)	1.4753	0.3610
	q_m (mg g ⁻¹)	1.7310	0.4664
	K_L (L mg ⁻¹)	0.00314	1.6366
	R_L	0.1272	0.0211
Freundlich	R^2	0.9718	0.9737
	n	1.7352	3.0743
	K_F (L g ⁻¹)	0.0996	0.2098
	R^2	0.9806	0.9891
Temkin	K_T (L mg ⁻¹)	0.1755	4.65
	b_T (kJ mol ⁻¹)	7.4481	16.8746
	R^2	0.9224	0.9700

The Temkin isotherm takes into accounts the effects of interaction of sorbate and sorbed species. The heat of sorption of all the molecules on the sorbent surface layer would decrease linearly with coverage due to sorbate-sorbate interactions (Oladoja et al., 2008). The linear form of the Temkin isotherm can be expressed as:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \quad (6)$$

where K_T (L mg⁻¹) is the equilibrium binding constant, corresponding to the maximum binding energy, b_T (J mol⁻¹) is a constant related to the heat of sorption, R is the gas constant (8.314 J mol⁻¹) and T is the absolute temperature (K) (Han et al., 2005). The values of the Temkin constants and correlation coefficients are presented in (tab 1). The correlation coefficient values did not show a good agreement with the experimental data for both pollutants.

CONCLUSIONS

Sorption of Acid orange 7 and Erythrosine B onto soil is dependent on initial concentration of the dyes, soil amount and contact time.

A detailed isotherm analysis of experimental data was carried out to determine the best isotherm models for the sets of equilibrium data for AO7 and EB on Iasi area soil. The experimental results were analyzed using three two-parameter adsorption isotherm models - the Langmuir, Freundlich and Temkin isotherms. Evaluating the correlation coefficients from the isotherm equations the analytical data showed that the Freundlich isotherm offers the best fit of the data, also, the Langmuir isotherm described the data more appropriate than Temkin isotherms.

Acknowledgements

This research was financially supported by the Ministry of Education and Research of Romania, in the frame of the National Program of Research, Development and Innovation, PNCDI - II, Program IDEI, Project ID_595, Contract 132/2007, and BRAIN project ID 6681, financed by the European Social Found and Romanian Government.

BIBLIOGRAPHY

- Han, R., Zhang, J., Zou, W., Shi, J., Liu, H., 2005 - *Equilibrium biosorption isotherm for lead ion on chaff*, J. Haz. Mat., vol. B 125, p. 266-271.
- Jarvis, N.J., Taylor, A., Larsbo, M., Etana, A., Rosén, K., 2010 - *Modelling the effects of bioturbation on the re-distribution of ¹³⁷Cs in an undisturbed grassland soil*, Eur J Soil Sci, vol. 61, p. 24-34.
- Mohamed, A.F., Yaacob, W.Z.W., Taha, M.H., Samsudin A.R., 2009 - *Groundwater and Soil Vulnerability in the Langat Basin Malaysia*, European Journal of Scientific Research, Vol.27, p.628-635.
- Oladoja, A.N., Aboluwoye, C.O., Oladimeji, Y.B., 2008 - *Kinetics and isotherm studies on methylene blue adsorption onto ground palm kernel coat*, Turkish Journal Engineering Environmental Science, vol.32, p. 303-312.
- Pan, X., Zhang, D., 2009 - *Removal of malachite green from water by Firmiana simplex wood fiber*, Electron. J. Biotechnol., vol.12, no. 4.
- Smaranda, C., Bulgariu, D., Gavrilă, M., 2009 - *An investigation of the sorption of Acid Orange 7 from aqueous solution onto soil*, Env. Eng. Manag J., vol. 8, p. 1391-1402.
- Wong, Y.C., Szeto, Y.S., Cheung, W.H., McKay, G., 2008 - *Effect of temperature, particle size and percentage deacetylation on the adsorption of acid dyes on chitosan*, Adsorption, vol.14, p. 11-20.