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Adsorption-desorption of methylene blue dye onto marine sediments: Kinetics and equilibrium studies

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Abstract

The present study concerns the investigation of the sorption and desorption phenomena of methylene blue (MB), which is an organic molecule used as a synthetic dye in several industries. For that purpose, the batch equilibrium technique was applied by using three marine sediments that were collected from the North Aegean Sea (Greece) and more specifically from unpolluted coasts of Chios island (sample S1), Lesvos island (S2 and S3). The criterion for the selection of those substrates as adsorbent surfaces were based on both their difference in their textural analysis (that ranged between 1.68–34.54%) and the content of organic matter as well (that varied from 1.70 to 5.38%). The obtained experimental results showed that both Freundlich and Langmuir isotherm models could describe the kinetics of the occurred process, whereas the correlation regression coefficients for the fit to that models were calculated to be $R^2 \geq 0.9004$ and $R^2 \geq 0.8487$, respectively. Furthermore, acquired results indicated a positive correlation between the sorption of MB and the organic matter content of marine sediments. Desorption studies revealed that the studied dye in some cases was adsorbed very weakly on sediments tested and hence was easily desorbed with seawater, while on the contrary in other cases MB was adsorbed very strongly on studied matrices with lower quantities of seawater extractable amounts.

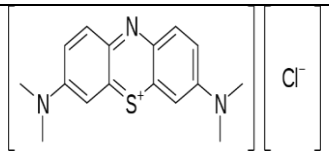
Keywords: Methylene blue, Synthetic dyes, Adsorption isotherms, Kinetics, Marine sediments

1. Introduction

Synthetic dyes are complex chemical substances that are manufactured from organic molecules and unquestionably have an important role in both industries (e.g. textile, plastic, paper, printing, etc.) and science (e.g. photo-redox catalysis, fluorescent tracers, medicinal applications, etc.). A wide variety of dyes, including aryl amines, azo dyes, anthraquinones, carbazoles, oxazines, phenothiazines, rhodamines, thiophene dyes, and several other chemicals that are classified to different chemical groups is used in numerous applications. Regardless of the various procedures that have been used worldwide to treat dye-containing wastewater produced by various industries (such as adsorption, precipitation, reverse osmosis, oxidation/reduction, and biological methods including aerobic and anaerobic treatments), dyes are inevitably released to the environment producing highly colored wastewater (according to the relevant scientific data, approximately 10%–15% of the originally used amount) [Koroglou et al., 2019]. Therefore, likewise many other anthropogenic organic substances, organic dyes can be introduced into various aquatic ecosystems including marine and coastal environments.

Methylene blue (MB) is the common name of [7-(Dimethylamino)phenothiazin-3-ylidene]-dimethylazanium chloride (IUPAC systemic name) (**Table 1**) that is typically used as a synthetic dye mainly by textile, paper and printing industries and as a medication to treat methemoglobinemia.

Table 1. Structural formulae, main physicochemical properties, and other information for MB

Data		Reference
Structural formulae		PubChem, 2013
Molecular formulae	$C_{16}H_{18}ClN_3S$	IARC, 2018
IUPAC systemic name	[7-(Dimethylamino)phenothiazin-3-ylidene]-dimethylazanium chloride	PubChem, 2013
Synonyms	Aizen methylene blue; Basic blue 9 (8CI); Calcozine blue ZF; Chromosmon; C.I. 52 015; Methylthionine chloride; Methylthioninium chloride; Phenothiazine5-ium,3,7-bis, (dimethylamino)-, chloride; Swiss blue; Tetramethylene blue; Tetramethyl thionine chloride	NTP, 2008; PubChem, 2013
Relative molecular mass	319.85	PubChem, 2013
Description	Dark green crystals or crystalline powder with bronze lustre, odourless, stable in air, deep blue solution in water or alcohol, forms double salts	PubChem, 2013
Density	1.0 g/mL at 20 °C	ChemNet, 2013
Solubility	43.6 g/L in water at 25 °C; also soluble in ethanol	PubChem, 2013
Vapour pressure	1.30×10^{-7} mm Hg at 25 °C	PubChem, 2013

Based on the extended published bibliographic information gathered within the present research it becomes obvious that an enormous scientific interest has been focused on the removal of MB dye as a pollutant from aqueous solutions by the performance of adsorption techniques onto low-cost adsorbents [Rafatullah et al., 2010] such as agricultural wastes, industrial solid wastes, biomass, clays minerals, and zeolites [Wang et al., 2022, Kuang et al., 2020].

On the contrary, there is a complete lack of data regarding the sorption process in water systems and specifically in marine and coastal ecosystems. Hence, the purpose of the present work was to investigate the sorption/desorption behavior of MB onto marine sediments to investigate its environmental fate after the entrance of the pollutant into the marine environment.

The present study is a study concerning the sorption-desorption behavior of methylene blue (MB) on marine sediments from three different areas of the North Aegean Sea.

2. Methods and materials

Sediment samples were collected from three different sampling stations of the Aegean Sea in Northern Greece (stations 1 and 2 were located in relatively unpolluted coastal areas of Chios and Lesvos islands, respectively, and station 3 was located in aquaculture (Selonda, Gera's Golf, Lesvos). The samples, prior to their use, were air-dried at room temperature, passed through a 10-mesh sieve (2mm particle size), and kept in dark Pyrex vials, tightly sealed, and under refrigeration (at -20 ºC). The % content of sediments' organic matter was determined by wet oxidation with $K_2Cr_2O_7$ in acidic pH, according to the Walkley-Black method [Walkley and Black, 1934]. The organic matter content was calculated by multiplying organic carbon by 1.72 [Vagi et al., 2010] The characteristics of different marine sediments employed in the present study are given in **Table 2**.

Table 2. Characteristics of the studied sediments

Sediment sample	Organic matter (%)	Textural analysis (%)	
		63-2000 μm	<63μm
S1	2.94	98.32	1.68
S2	1.70	93.76	6.24
S3	5.38	65.46	34.54

Analytical grade methylene blue (MB) was supplied by Merck (Germany) and used as adsorbate without any further purification.

The seawater used in the current study was collected from an unpolluted area of the Aegean Sea, nearby the city of Mytilene (Lesvos).

The batch adsorption experiments were conducted according to the Organization for Economic Co-operation and Development Guideline 106 [OECD, 2000]. Seven solutions of MB dye prepared in seawater and with final concentrations that ranged between the values of 5 and 100 mg L^{-1} were used for all tested adsorption systems. Each mixture consisted of 1 g of sediment mixed with 45 mL of MB solution in a 250 mL Erlenmayer flask and sealed with screw caps with Teflon lining. The fact that adsorption equilibrium was reached within 2 h (according to the results of preliminary kinetic experiments) defined that mixtures contained in flaks should be shaken for 2 h to achieve equilibrium. Therefore, a horizontal shaker (Gesellschaft für Labortechnik, GFL, Germany) was used and the procedure was conducted at a constant room temperature of 21± 0.5ºC. Aliquots of 5 mL of the aquatic suspensions were withdrawn (after achieving adsorption equilibration), and centrifuged at 5000 rpm for 15 min (Heraeus, Germany). Finally, the quantity of MB that had been adsorbed by the marine sediments was evaluated from the difference between the initial and equilibrium dye concentration in the solution. Simultaneously, one blank (without MB) and one control (without sediment) were included in each sample batch to assure the quality control of the experiments.

Desorption of MB at 21± 0.5 ºC was determined by using the experimental systems from previously conducted batch adsorption tests. After the initial equilibration of 1 g of the soil sample with 45 mL of MB solution the sediment/seawater mixtures were centrifuged the supernatant was poured off and replaced by the same volume of fresh seawater. The flasks were mechanically shaken for 2 h in order to achieve the desorption equilibration process and centrifuged (5000 rpm for 15 min). In each case, the amount of dye recovered through the desorption process by seawater was determined by spectrometric analysis, whereas the amount of MB remaining adsorbed by the sediment was calculated as the difference between the initial adsorbed amount and the desorbed amount [Vagi et al., 2010].

3. Results and conclusions

Adsorption isotherms and kinetic experiments

The rate of adsorption of MB onto marine sediments was determined by the agitation of the MB seawater-sediment mixtures for respectively 10, 20, 30, 60, 120, and 360 min. Data for the rate of sorption of a 7 mg/L solution of MB by 0,5 g/L of the two sediments (specifically S1 and S3) are shown in **Figure 1**. The sorption of MB is a fast phenomenon; under the conditions of the experiment, all systems achieved equilibrium within 2 hours of contact time. The amount of MB degraded during this time is negligible as indicated by the blank experiment of MB in seawater without the addition of sediment.

Adsorption isotherm models and coefficients

The acquired sorption data depicted in **Figure 2** were fitted to the Freundlich and Langmuir isotherm models, described by Equations (1, 2) and (3) respectively, which were used to calculate the isotherm constants and maximum adsorption capacity of MB on various sediments employed in the study:

$$\frac{x}{m} = C_s = K_F\, C_e^{1/n}$$

$$\log\frac{x}{m} = \log C_s = \log K_F + \frac{1}{n}\log C_e$$

$$q = \frac{q_{max}\, b\, C_e}{1 + b\, C_e}$$

where x/m = C_s = q (in mg g^{-1}) is the quantity of dye adsorbed (x, in mg) per unit mass of adsorbent (m, in g); C_e (in mg L^{-1}) is the equilibrium concentration of MB in solution; K_F is the adsorption constant or distribution coefficient that represents the quantity of MB adsorbed in mg/g (sediment) for a unit equilibrium concentration of the compound under test; n represents energy distribution of sorption sites, while l/n is a measure for the sorption intensity (e.g. for n=l the partition between the two phases is independent of the concentrations); $(x/m)_{max} = q_{max}$ (in mg g^{-1}) is the measure of monolayer (maximum) adsorption capacity of the adsorbent substrate (marine sediment); and finally b is Langmuir constant and represents the energy of adsorption (in g/L).

Based on the experimental data of the present study it is obvious that both isotherm models used fitted the experimental data reasonably well and the results are summarised in **Table 3**. However, the correlation coefficient values (R^2) show that the data fitted better with Freundlich isotherm model (R^2 ≥0.9004) than Langmuir model (R^2≥ 0.8487).

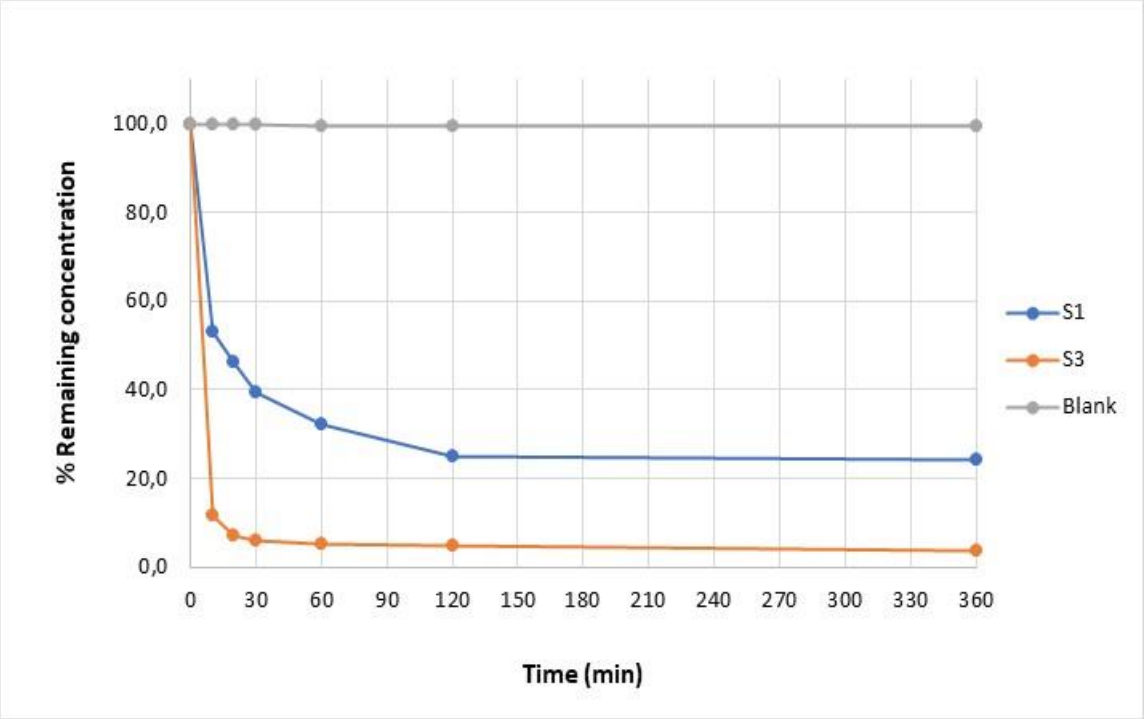


Figure 1. Rate of sorption of MB onto marine sediments studied.

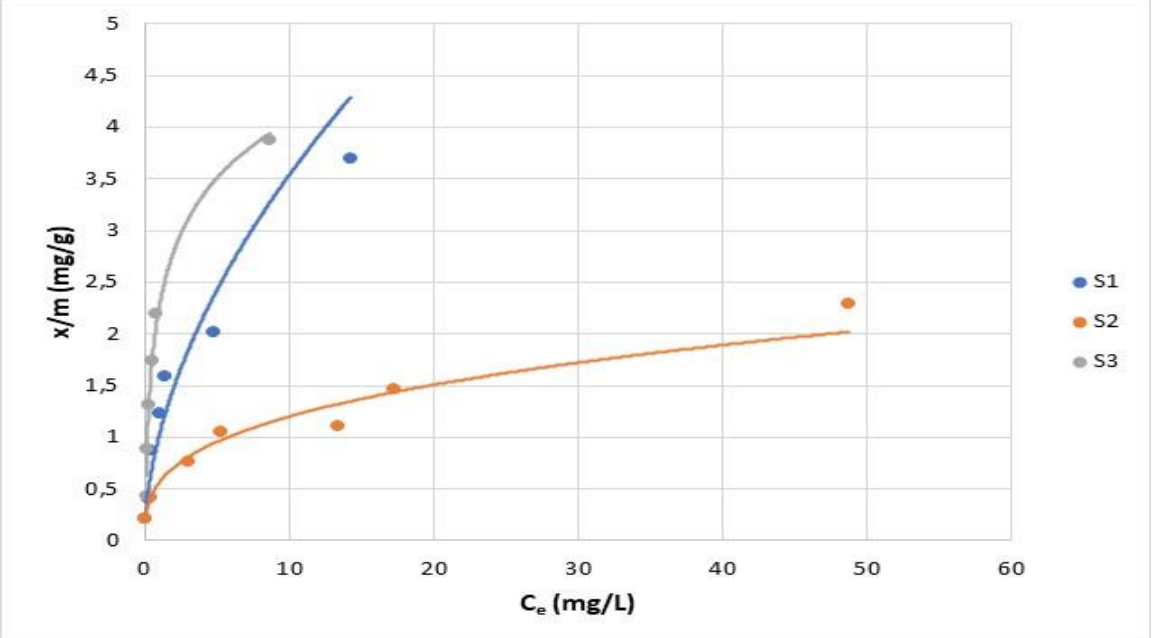


Figure 2. Adsorption isotherms of MB onto marine sediments of the study.

Table 3. The adsorption isotherm constants of selected pesticides OPPs on different soils by Langmuir and Freundlich models.

	Freundlich isotherm model						Langmuir isotherm model		
	$\frac{x}{m} = C_s = K_F C_e^{1/n}$			$\log\frac{x}{m} = \log C_s = \log K_F + \frac{1}{n}\log C_e$			$q = \frac{q_{max} b C_e}{1 + b C_e}$		
Sediment sample	**K_F (mL g^{-1})**	**n**	**R^2**	**K_F (mL g^{-1})**	**n**	**R^2**	**q_{max} (mg g^{-1})**	**b**	**R^2**
S1	1.0049	1.8315	0.9659	1.0048	1.8315	0.9444	2.5907	6.2246	0.9829
S2	0.5623	3.0414	0.9644	0.5623	3.0414	0.9841	0.9827	6.1419	0.8884
S3	1.8576	2.2267	0.9004	1.8578	2.2267	0.8255	6.7981	30.6359	0.8487

The K_F values obtained were different for each adsorption system of MB and sediment. More specifically, estimated values of Freundlich sorption coefficients K_F for S1, S2, and S3 sediments respectively were 1.0049, 0.5623, and 1.8576. In all three cases of marine sediment samples tested the K_F (Freundlich isotherm model) and q_{max} (Langmuir isotherm model) values are in the order: $S_3>S_1>S_2$ (**Table 3**), while % content of organic matter of the adsorbent sediments is in the order: $S_3>S_1>S_2$ (**Table 2**). The amount of MB sorbed on sediment with lower content of organic matter (S2) was the smallest. However, for sediments with the highest organic matter content (S1, 2.94, and S3, 5.38%), sorption follows a different behavior. A positive correlation between the sorption of MB and the organic matter content of marine sediments is indicated.

Desorption process

Desorption of MB that was accomplished by seawater (data not shown) indicated the variable extent of reversibility of the sorption phenomenon in each studied case. In other words, the desorbed quantities of MB were different in each system of seawater/marine sediment system that was examined, and dependable on the properties of the adsorbent sediment.

References

ChemNet (2013), Methylene blue. Royal Society of Chemistry. Available from: http://chemnet.rsc.org.

International Agency for Research on Cancer (IARC) (2018), Monographs on the identification of Available from: https://monographs.iarc.who.int/wp-content/uploads/2018/06/mono108-06.pdf

Fytianos K., Voudrias E., Mouratidou Th. (1998), The sorption-desorption behavior of linear alkylbenzene sulfonate in marine sediments, *Chemosphere*, **36(9)**, 2067-2074.

Koroglu E.O., Yoruklu H.C., Demir A., Ozkaya B. (2019), Chapter 3.9 - Scale-Up and Commercialization Issues of the MFCs: Challenges and Implications, Editor(s): S. Venkata Mohan, Sunita Varjani, Ashok Pandey, In *Biomass, Biofuels and Biochemicals, Microbial Electrochemical Technology*, Elsevier, pages 565-583, ISBN 9780444640529, Available from: https://doi.org/10.1016/B978-0-444-64052-9.00023-6.

Kuang Y., Zhang X. and Zhou S. (2020), Adsorption of methylene blue in water onto activated carbon by surfactant modification. *Water*, **12(2)**, 587.

National Toxicology Program(NTP) (2008), Toxicology and carcinogenesis studies of methylene blue trihydrate (Cas No. 7220–79–3) in F344/N rats and B6C3F1 mice (gavage studies), *Natl Toxicol Program Tech Rep Ser*, **540**, 1–224. PMID:18685714

Organization for Economic Co-operation and Development (OECD), in OECD Guidelines for Testing of Chemicals – Test Guideline 106: Adsorption-desorption in Soils, edited by OECD Publications Office – Environ. Health and Safety Div. (OECD Environ. Directorate, Paris, France, 2000). Available from: https://doi.org/10.1787/9789264069602-en

PubChem (2013). Methylene blue. Pubchem database. National Center for Biotechnology Information. Available from: https://pubchem.ncbi.nlm.nih.gov/ [online database].

Rafatullah M., Sulaimana O., Hashima R. and Ahmadb A. (2010) Adsorption of methylene blue on low-cost adsorbents: A review. *Journal of Hazardous Materials*, **177**, 70–80.

Vagi M.C., Petsas A.S., Kostopoulou M.N. and Lekkas T.D. (2010), Adsorption and desorption processes of the organophosphorus pesticides, dimethoate and fenthion, onto three Greek agricultural soils, *International Journal of Environmental and Analytical Chemistry*, **90**(3-6), 369-389.

Walkley A. and Black I.A. (1934), An examination of the Degtjiareff method for determining soil organic matter and a proposed modification of chromic acid titration method, *Soil Science*, **37**, 29-38.

Wang J.; Ma J.; Sun Y. (2022), Adsorption of methylene blue by coal-based activated carbon in high-salt wastewater, *Water*, **14(21)**, 3576.