

Original Research

**SORPTION OF TEXTILE DYES ONTO BISMUTH-MODIFIED WOOD WASTE
SORBENT: KINETIC AND EQUILIBRIUM ANALYSIS**

DOI: 10.5937/EcoTER26279V

**Nena Velinov Georgiev^{1,a*}, Miljana Radović Vučić^{1,b}, Milica Petrović^{1,c}, Miloš Kostić^{1,d},
Milan Momčilović^{1,e}, Jelena Mitrović^{1,f}, Aleksandar Bojić^{1,g}**

¹ University of Niš, Faculty of Science and Mathematics, Department of Chemistry, Višegradska 33,
18 000 Niš, SERBIA

^a <https://orcid.org/0000-0001-9043-8521> ^b <https://orcid.org/0000-0001-6820-5844>

^c <https://orcid.org/0000-0002-7537-0327> ^d <https://orcid.org/0000-0001-6488-5184>

^e <https://orcid.org/0000-0001-5370-0148> ^f <https://orcid.org/0000-0001-9634-7727>

^g <https://orcid.org/0000-0002-9853-2747>

Abstract

Textile dye contamination in aquatic environments represents a major ecological issue due to its persistence, harmful effects on aquatic organisms, and possible risks to human health. In this work, wood waste modified with bismuth was evaluated as a low-cost sorbent for the removal of textile dyes Reactive orange 16 from water. Sorption behaviour was examined through kinetic and equilibrium analyses in order to better understand the interaction between the dye molecules and the sorbent surface. The obtained results were best described by the pseudo-second-order kinetic model and the Langmuir isotherm model ($r^2 \geq 0.99$), indicating predominantly monolayer sorption on homogeneous active sites. The prepared material exhibited a maximum sorption capacity of 415.22 mg/g, highlighting its potential application as an effective and sustainable sorbent for wastewater treatment.

Keywords: wood waste, modification, bismuth, sorption, textile dye.

INTRODUCTION

Water pollution represents one of the major environmental challenges due to its harmful effects on ecosystems and human health [1]. Among various pollutants, textile dyes are of particular concern because of their extensive industrial use, complex chemical structure, and resistance to natural degradation processes [2]. The discharge of untreated dye-containing wastewater into aquatic environments can reduce light penetration, disturb aquatic life, and introduce potentially toxic or mutagenic compounds into the ecosystem [3].

Conventional wastewater treatment methods are often insufficient for efficient dye removal, while advanced techniques may require high operational costs and complex infrastructure [4]. In recent years, sorption has gained attention as an efficient, economical, and environmentally friendly approach for wastewater treatment [5]. Waste-derived materials, such as wood waste, are especially promising sorbents due to their abundance, low cost, and presence of functional groups capable of binding pollutants.

* nena.velinov@yahoo.com; nena.velinov@pmf.edu.rs

Therefore, this study focused on the preparation of a bismuth-modified wood waste sorbent and the investigation of its potential for the removal of Reactive orange 16 dye through kinetic and equilibrium sorption analyses.

MATERIALS AND METHODS

Reagents

Reactive orange 16 was obtained from Sigma-Aldrich (USA) and used without any purification. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, HNO_3 and NaOH were of analytical grade and purchased from Merck (Germany).

Sorbent preparation

Wood waste used in this study was obtained from a furniture production facility located in Eastern Serbia. The collected sawdust was initially sieved, and particles within the 0.4–0.8 mm size range were selected and thoroughly rinsed several times with deionized water. The material was subsequently treated with 0.5 M NaOH solution for 90 min in order to modify the surface properties, followed by repeated washing with deionized water until the filtrate reached approximately neutral pH. For the chemical modification, 10 g of the pretreated sawdust was introduced into a solution containing 2.0 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ dissolved in 30.0 cm^3 of 2 M HNO_3 . The suspension was stirred for 30 min, after which the solid phase was separated by filtration, rinsed four times with ultrapure water, and dried at 55.0 °C for 120 min.

Procedure

Fresh working solutions of the textile dye were prepared daily by dilution of the stock solution (1.00 g/dm^3). Sorption experiments were performed by contacting the dye solutions with the sorbent at a concentration of 2.0 g/dm^3 under acidic conditions (pH 2.0). The pH of the mixtures was adjusted using NaOH and HNO_3 solutions. Samples of the dye solution were collected prior to sorption (0 min) and at predetermined time intervals of 1, 5, 10, 20, 40, 60, 90, 120, and 180 min. The residual dye concentration in the solutions was determined spectrophotometrically at 495 nm using a Shimadzu UV-1800 spectrophotometer. The amount of dye sorbed at time t , expressed as q_t (mg/g), was calculated according to the following equation:

$$q_t = \frac{(c_0 - c_t) \cdot V}{m} \quad (1)$$

where c_0 and c_t are the starting and final concentrations of the dye (mg/dm^3), respectively, V is volume of the solution (dm^3) and m is mass of the sorbent (g).

Sorption modelling

Kinetic and equilibrium experiments were performed using initial dye concentrations ranging from 10.0 to 500.0 mg/dm^3 , while the sorbent dosage was maintained at 2.0 g/dm^3 . To evaluate the sorption behavior of the prepared material, pseudo-first-order [7] and pseudo-second-order [8] kinetic models were employed for the analysis of sorption kinetics. Equilibrium data were further interpreted using the Langmuir [9], Freundlich [10], and Sips

[11] isotherm models. The nonlinear forms of the applied kinetic and isotherm equations (Table 1 and Table 2) were used for the calculation of sorption parameters, as nonlinear modeling provides a more accurate representation of the experimental data compared to linearized approaches.

RESULTS AND DISCUSSION

Kinetic study

The experimental results and calculated parameters obtained from the pseudo-first-order and pseudo-second-order kinetic models are shown in Table 1.

Table 1 Kinetic parameters for dye sorption onto bismuth-modified wood waste

Model	Equation	Parameter	Value			
Experimental		c_0^a	50.0	100.0	250.0	500.0
		$q_{e, \text{exp}}^b$	25.0	49.99	124.97	249.89
Pseudo-first order	$q_t = q_e(1 - e^{-k_1 t})$	$q_{e, \text{cal}}^c$	24.97	49.62	122.22	234.87
		k_1^d	2.67	1.06	0.64	0.15
		r^2	0.997	0.994	0.980	0.965
Pseudo-second order	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	$q_{e, \text{cal}}^c$	25.0	50.0	125.01	250.03
		k_2^e	4.08	1.96	1.05	0.27
		r^2	0.999	0.999	0.999	0.998

^a c_0 – initial concentrations of the dye (mg/dm³)

^b $q_{e, \text{exp}}$ – experimental equilibrium sorption capacities (mg/g)

^c $q_{e, \text{cal}}$ – calculated sorption capacities (mg/g)

^d k_1 – pseudo-first order rate constants (1/min),

^e k_2 – pseudo-first order rate constants (g/mg·min)

The equilibrium sorption capacities (q_e) predicted by both the pseudo-first-order and pseudo-second-order kinetic models were generally consistent with the experimentally determined values. However, the pseudo-second-order model provided q_e values that were in closer agreement with the experimental data and exhibited higher correlation coefficients ($r^2 = 0.998$ – 0.999) compared to the pseudo-first-order model ($r^2 = 0.965$ – 0.997). The pseudo-first-order model adequately described the sorption process at lower dye concentrations, where a large number of available active sites existed on the sorbent surface. In contrast, at higher concentrations, the applicability of this model decreased due to progressive occupation and saturation of the active sorption sites. The obtained results indicate that the pseudo-second-order kinetic model provides a better fit for the experimental data compared to the pseudo-first-order model in the case of dye sorption onto the bismuth-modified wood waste. This is supported by higher correlation coefficients and by the fact that the calculated q_e values are in closer agreement with the experimentally determined ones across all tested conditions.

Therefore, the pseudo-second-order model can be considered more appropriate for describing the investigated sorption system. These findings suggest that the sorption process depends on the concentration of dye in solution as well as on the amount accumulated on the sorbent surface at equilibrium. The rate-controlling step is likely associated with interactions involving electron sharing or exchange between the sorbent surface and dye molecules [12].

Equilibrium study

The calculated parameters obtained from the application of the Langmuir, Freundlich, and Sips isotherm models, together with the corresponding experimental results, are presented in Table 2.

Table 2 Isotherm parameters for dye sorption onto bismuth-modified wood waste

Model	Equation	Parameter	Value
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{q_m^c}{K_L^d}$	415.22
		r^2	0.999
		K_F^e	225.21
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	n_F^f	6.58
		r^2	0.877
		$\frac{q_m}{K_S^g}$	416.32
Sips	$q_e = \frac{q_m K_S C_e^{1/n}}{1 + K_S C_e^{1/n}}$	K_S^g	3.857
		n_S^h	0.99
		r^2	0.998

^c q_m – maximal sorbent capacity (mg/g), ^d K_L – Langmuir constant (dm³/mg)

^e K_F – Freundlich constant (dm³/mg), ^f $1/n_F$ – Freundlich exponent

^g K_S – Sips constant (dm³/mg), ^h $1/n_S$ – Sips exponent

The Langmuir isotherm model showed the best agreement with the experimental data, with correlation coefficients exceeding 0.99, indicating that it describes dye sorption onto the bismuth-modified wood waste more accurately than the Freundlich model, which exhibited a lower r^2 value (0.877). This suggests that the sorption process predominantly occurs as monolayer coverage on a finite number of homogeneous active sites, with no further uptake once saturation is reached. The maximum sorption capacity estimated from the Langmuir model was 415.22 mg g⁻¹ (Table 2).

In contrast, the Freundlich model did not adequately represent the experimental data due to its lower correlation coefficient, although the value of the Freundlich exponent ($n_F = 6.58$) indicates favourable sorption conditions, as it falls within the range of 1 to 10, suggesting a generally favourable interaction between sorbate and sorbent.

The Sips isotherm model also provided an excellent fit to the experimental data, with a high correlation coefficient ($r^2 = 0.998$) and a calculated equilibrium sorption capacity (416.32 mg g⁻¹) that closely matched the experimentally obtained value (Table 2). This confirms that the Sips model adequately describes dye sorption onto the bismuth-modified wood waste. As a hybrid model combining the Langmuir and Freundlich approaches, the Sips equation behaves like the Freundlich model at lower concentrations, while at higher concentrations it converges toward the Langmuir model, accounting for monolayer sorption on a finite number of active sites. The heterogeneity factor ($n_S = 0.99$) being close to unity indicates that the sorbent surface is nearly homogeneous. In practical terms, this suggests that the system behaviour approaches the Langmuir model, meaning that the equilibrium data can be effectively described by monolayer sorption assumptions [13].

CONCLUSION

A novel bismuth-modified wood waste sorbent was successfully synthesized and used for textile dye removal. The kinetic study revealed that dye sorption onto the prepared material follows the pseudo-second-order model, indicating that the process depends on both the concentration of dye in solution and the amount accumulated on the sorbent surface at equilibrium. Equilibrium data were best described by the Langmuir isotherm model, suggesting monolayer coverage on a homogeneous surface. The maximum sorption capacity of the bismuth-modified wood waste was determined to be 415.22 mg g^{-1} , demonstrating its potential applicability as an effective material for dye removal from aqueous solutions.

ACKNOWLEDGEMENT

The authors would like to acknowledge financial support from the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Agreement No 451-03-33/2026-03/200124 and 451-03-34/2026-03/200124).

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