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REMOVAL OF REACTIVE BLUE 13 USING MODIFIED
CELLULOSIC MATERIAL BASED ON RICE HUSKS

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Abstract

The present study deals with the removal efficiency regarding Reactive Blue 13 (RB) of a cationized cellulosic adsorbent prepared from agricultural waste. The rice husks were used as a raw material to extract and separate the cellulose by alkali and bleaching treatment. The cellulosic material was modified with N, N-dimethyl-1-octadecylamine to prepare a cationized adsorbent. The adsorption process was scrutinized across multiple parameters influencing dye removal and was well described by pseudo-second-order and Langmuir models predicting chemically rate-controlled monolayer adsorption. Thermodynamic studies show that the adsorption of RB is spontaneous and endothermic. It was established that the new cationized cellulosic material could serve as an effective adsorbent for the removal of RB from aqueous media.

Key words: Reactive Blue 13, rice husks, adsorption, cellulose

Introduction. The removal of dyes from wastewater is a critical and challenging environmental issue. Reactive dyes, which chemically bond to fibres during the dyeing process via covalent bonds, are especially popular due to their excellent colour fastness and durability. These dyes are commonly used for successfully dyeing cotton, viscose, wool, silk, and other natural and synthetic fibres. One example of these dyes is Reactive Blue 13 (RB), a synthetic dye known for producing popular shades like blue and navy. A major challenge with reactive

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dyes is that typically 60–70% remain unutilized during the dyeing process, resulting in significant amounts of coloured wastewater [1]. This issue is exacerbated by the high water solubility of dyes like RB, which leads to considerable residue during the fixation process. Reactive azo dyes contain azo bonds ($-N=N-$), which give them their colour but also make the resulting wastewater toxic, mutagenic, and carcinogenic to humans and animals [2]. Given these serious environmental impacts, many researchers are actively seeking effective, eco-friendly methods to remove reactive dyes from wastewater. Various techniques have been explored for water decontamination, with adsorption being widely used due to its versatility and efficiency. However, the high cost of commercial adsorbents and the losses during their regeneration limit their broader use, driving interest in low-cost natural materials as alternative adsorbents. Renewable agricultural residues, which are produced on a large scale as waste, offer a promising solution. Among the various agricultural wastes, rice husks (RH) hold a prominent position, not only due to their global abundance but also because of their distinctive chemical properties [3]. The cell walls of plant species like rice are primarily composed of nearly pure cellulose. Plant-derived cellulose, the most abundant biopolymer on Earth, has been shown to effectively adsorb a wide range of organic and inorganic pollutants from aqueous solutions, due to its abundant hydroxyl groups [4]. Cationized cellulose is produced by grafting cationic functional groups onto the cellulose hydroxyl groups. The modified materials function as anion exchangers, enhancing the adsorption of anionic pollutants via electrostatic attraction. The cationization process involves embedding amine or quaternary ammonium groups into the cellulose structure, further improving its adsorption capabilities [5].

Currently, only few studies have addressed the removal of the Reactive Blue dye through adsorption methods, including those using activated carbon [1], organo-bentonite [6], kaolin clay [7], and Fe_3O_4 loaded chitin [8]. This survey is focused on utilizing renewable, cellulose-rich agricultural resources as efficient adsorbents for reactive dyes and transforming them into value-added products with practical applications in environmental protection. Specifically, the adsorption potential of a rice husk-based material, modified with cationic groups, for the removal of Reactive Blue 13 from aqueous solutions was evaluated.

Experimental. Materials and chemicals. Rice husks from the 2022 harvest in Pazardzhik region, Bulgaria, were used. These husks were initially cleaned with deionized water and dried at 120 °C before being milled using a rotary mill. The resulting fraction with particles smaller than 0.63 mm was selected for the experiments. The cationic-modified material was prepared as described in the study by VASSILEVA et al. [9]. Briefly, the cellulose extraction from rice husks involved delignification and bleaching using NaOH and $NaClO_2$. Milled rice husks were treated with NaOH and $NaHSO_3$ at 90 °C, washed, and dried. The product was then bleached with $NaClO_2$ and acetic acid at 70 °C, washed, and dried again. The final cellulose was milled into a fine powder. The prepared cellulose sample

was treated with NaOH and epichlorohydrin, followed by treatment with a solution of N, N-dimethyl-1-octadecylamine in isopropanol. The sample was then washed and dried.

The porous structure of studied material was investigated by low-temperature (-196°C) nitrogen adsorption using a Quantachrome NOVA 1200 apparatus. Infrared spectra of the sample before and after RB adsorption were recorded using a Nicolet Avatar 360 FTIR spectrometer with a spectral resolution of 2 cm^{-1} and an accumulation of 64 scans.

Adsorption studies. Adsorption experiments were conducted using 50 mL conical flasks containing a predetermined quantity of adsorbent mixed with 10 mL of RB solution. These mixtures were then agitated on a rotary shaker for varying durations. Once equilibrium was reached, the mixture was separated by centrifugation, and the supernatant was analysed using a spectrophotometer (Vis DLAB SP-V1000, DLAB Scientific Malaysia SDN BHD) to measure absorbance at $\lambda_{\text{max}} = 566\text{ nm}$.

All reagents employed in the experiments were of analytical grade. Batch experiments were performed to explore how factors such as contact duration, pH level, initial dye concentration, and temperature affect the adsorption. The equilibrium adsorption capacity (Q_e , measured in mg g^{-1}) was calculated using the following equation

$$(1) \quad Q_e = (C_0 - C_e) \times V/m,$$

where C_0 and C_e represent the initial and equilibrium concentrations of RB (mg L^{-1}), respectively, V stands for the solution volume (L), and m corresponds to the mass of the sorbent (g). It is essential to note that each experiment was conducted in triplicate to ensure accuracy and reliability.

Results and discussion. The results from analysing the nitrogen adsorption-desorption isotherm of the studied material indicate that the specific surface area is $0.5\text{ m}^2\text{g}^{-1}$ and the total pore volume is $0.002\text{ cm}^3\text{g}^{-1}$. The sample exhibits a wide range of pore sizes, with mesopores being predominant. The average pore diameter is calculated to be 31 nm.

The pH of the solution is critical for effective dye removal. Experiments were conducted to optimize the solution pH by varying it from 2 to 10, using an initial dye concentration of 500 mg L^{-1} . Figure 1a illustrates the relationship between the amount of RB adsorbed and the initial pH. The results show that adsorption increases with decreasing pH, with the highest removal efficiency achieved at pH 2. Consequently, all subsequent experiments were carried out at this pH level. Reactive dyes tend to ionize significantly in aqueous solutions. Within the pH range of 2 to 8, the reactive dye's surface is negatively charged due to the presence of sulphonate groups (SO_3^-) [1]. At low pH levels, there is greater electrostatic attraction between the sulphonate groups of RB and the NH_3^+ groups of the cationized cellulosic material. In contrast, under alkaline conditions, the

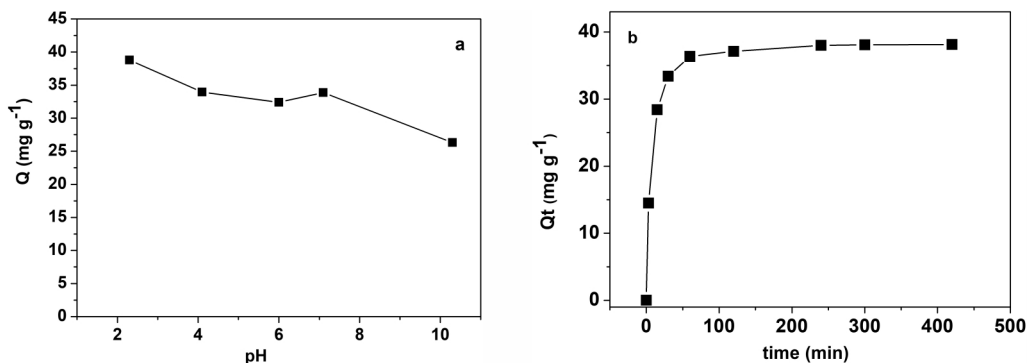


Fig. 1. Effect of pH (a) and contact time (b) on RB adsorption

presence of OH^- ions competes with the dye, reducing adsorption capacity. These findings are consistent with similar studies on RB adsorption [1, 7].

The effect of contact time was investigated at pH 2.0 with an initial RB concentration of 500 mg L^{-1} . Figure 1b illustrates how the adsorption capacity Q_e (mg g^{-1}) varies with contact time. The results indicate that the amount of RB adsorbed increased rapidly with longer agitation time and reached equilibrium after 60 min, demonstrating an efficient adsorption rate. To comprehend the adsorption mechanism, three kinetic models were utilized on the experimental data: the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. The specified models are expressed by the following equations:

1. Pseudo-first-order model:

$$(2) \quad \log(Q_e - Q_t) = \log(Q_e) - (k_1/2.303)t.$$

2. Pseudo-second-order model:

$$(3) \quad (t/Q_t) = (1/k_2Q_e) + (1/Q_e)t.$$

3. Intraparticle diffusion model:

$$(4) \quad Q_t = k_{id}t^{1/2} + C.$$

In these equations, Q_e and Q_t represent the amounts of RB adsorbed at equilibrium and at time t , respectively, while k_1 , k_2 , and k_{id} are the rate constants specific to each model. Additionally, C is a constant associated with the boundary layer thickness. The calculated rate constants and correlation coefficients (r^2) are presented in Table 1. A comparison between the pseudo-first-order and pseudo-second-order kinetic models reveals that the adsorption of RB dye onto the studied adsorbent aligns more closely with pseudo-second-order kinetics. Analysis of the

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Kinetic parameters and isotherm constants for RB adsorption

Pseudo-first order constants			Pseudo-second order constants			Intra-particle diffusion constants		
Q_e (mg g ⁻¹)	k_1 (min ⁻¹)	r^2	Q_e (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	r^2	K_{id} (mg g ⁻¹ min ^{-1/2})	C (mg g ⁻¹)	r^2
3.18	0.005	0.9368	38.60	0.217	0.9999	3.575 0.1460	11.26 35.42	0.9423 0.9481
Langmuir parameters ¹			Freundlich parameters ²			Dubinin-Radushkevich parameters ³		
Q_0 (mg g ⁻¹)	K_1 (L mg ⁻¹)	r^2	k_F (mg ¹⁻ⁿ L ⁿ g ⁻¹)	n (L mg ⁻¹)	r^2	Q_m (mg g ⁻¹)	E (kJ mol ⁻¹)	r^2
53.16	0.024	0.9996	6.07	2.97	0.9716	39.25	0.82	0.8335

¹ $C_e/Q_e = 1/K_L Q_0 + C_e/Q_0$; ² $\ln Q_e = \ln k_F + (1/n) \ln C_e$; ³ $\ln Q_e = \ln Q_m - \beta \varepsilon^2$, $\varepsilon = RT \ln(1 + 1/C_e)$, $E = 1/(-2\beta)^{1/2}$

intraparticle diffusion model suggests that the adsorption process involves multiple stages. The kinetic plot (figure not shown) exhibits two distinct linear regions, indicating a complex adsorption mechanism. The results clearly show that diffusion is not the limiting factor in the rate of RB adsorption. This suggests that the adsorption process is influenced by both the concentration of RB molecules in the solution and the number of available adsorption sites on the adsorbent surface [10]. Furthermore, chemical reactions appear to play a crucial role in controlling the speed of this process.

Adsorption isotherms describe the relationship between the amount of adsorbate on the adsorbent surface and its concentration in the solution at equilibrium. These models help to understand how adsorbates interact with the adsorbent and predict the adsorption capacity. The experimental RB adsorption isotherm for the investigated material are presented in Fig. 2. In the present study, the equilibrium data for dye RB molecules were analyzed using three prominent isotherm models: Langmuir, Freundlich, and Dubinin–Radushkevich. The specified models, whose equations are formulated based on different principles are described in [11]. The Langmuir isotherm assumes a monolayer adsorption on a surface with a finite number of identical sites. It is best suited for processes where adsorption occurs uniformly on the adsorbent surface with no interaction between adsorbed molecules. The Freundlich isotherm is an empirical model that describes adsorption on heterogeneous surfaces with a non-uniform distribution of adsorption heat. The Dubinin–Radushkevich isotherm is used to describe adsorption on porous materials and accounts for the potential energy in the pores. It is particularly useful for distinguishing between physical and chemical adsorption processes,

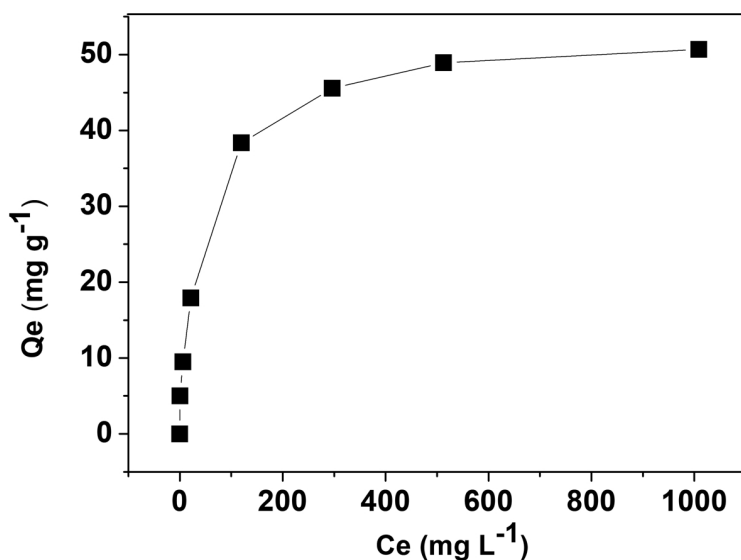


Fig. 2. Adsorption isotherm toward RB

as it provides information about the adsorption mechanism. The isotherm constants and correlation coefficients shown in Table 1, indicate that RB adsorption is best described by the Langmuir isotherm model. This is supported by the exceptionally high correlation coefficient, which is higher than those derived from the Freundlich and Dubinin–Radushkevich models. These results suggest that the primary mechanism of RB adsorption involves binding to a relatively uniform surface and the formation of a monolayer. The equilibrium adsorption capacity was determined to be 53.16 mg g⁻¹. Notably, this adsorption capacity for RB is comparable to values reported in the literature, highlighting the material's suitability for RB removal from aqueous solutions [1, 7, 8]. The n -value of 6.07 indicates favourable adsorption onto the studied material [12]. The Dubinin–Radushkevich isotherm model provides insight into the adsorption energy, with the calculated mean free energy being 0.82 kJ mol⁻¹. These results suggest that physisorption is likely the dominant adsorption mechanism.

To evaluate the effect of temperature on RB removal, experiments were conducted at 293 K, 303 K, and 333 K. The results showed that the amount of RB adsorbed increased with temperature, indicating an endothermic process. The distribution coefficient, K_d , and the thermodynamic parameters can be described by the following equations:

$$(5) \quad K_d = Q_e/C_e,$$

$$(6) \quad \ln K_d = \Delta S^0/R - \Delta H^0/RT,$$

where K_d is the equilibrium constant, R represents the gas constant (measured in J mol⁻¹K⁻¹), and T denotes the temperature (measured in Kelvin). By plotting $\ln K_d$ against $1/T$, the enthalpy change ΔH^0 can be derived from the slope, and the entropy change ΔS^0 from the intercept. The negative ΔG^0 values (−9.63, −11.55, and −13.47 kJ mol⁻¹ at 293 K, 313 K, and 333 K, respectively) confirm that RB dye adsorption is both feasible and spontaneous. As these free energy values fall within the range of 0 to −20 kJ mol⁻¹, physisorption is identified as the dominant mechanism. Additionally, the positive ΔH^0 (18.50 kJ mol⁻¹) further supports the conclusion that adsorption is primarily physical and increases with temperature. The positive entropy change ($\Delta S^0 = 95.44 \text{ J mol}^{-1} \cdot \text{K}^{-1}$) suggests a reduction in molecular order at the solid-liquid interface, allowing greater freedom for the adsorbed dye molecules. The small positive ΔS^0 indicates minimal structural changes on the adsorbent surface during adsorption.

The regeneration of the adsorbent and the disposal of adsorbate-loaded adsorbent are critical considerations for sustainable dye removal processes. Desorption enhances the eco-friendliness of the process by enabling reuse of the adsorbent. Therefore, desorption of Reactive Blue dye was conducted in a batch system using 1 M NaOH as the eluent. A measured amount of the pre-adsorbed material was added to 10 mL of 1 M NaOH and stirred for 24 h. Afterward, the eluent was

filtered and analyzed to quantify the desorbed dye. The results demonstrated a high recovery efficiency of 85%, indicating that the adsorbent material can be effectively regenerated and reused for further adsorption cycles, making the process both economical and environmentally beneficial.

FTIR spectroscopy was employed to identify the functional groups in the cationized cellulosic material responsible for dye sorption. Figure 3 displays the IR spectra before and after RB adsorption. The presence of different functional groups such as -OH , COOH , -C-O-C , etc. makes the shape of spectra bands broader and more complex due to the hydrogen bonds and conformational structure of material. Both spectra show characteristic cellulose absorption bands at approximately 1060 cm^{-1} and 1422 cm^{-1} , corresponding to the stretching vibrations of the OH and C-O groups in the glucosidic chains of the polysaccharide [9]. A band at 1265 cm^{-1} , related to vibrations of the aromatic rings. Additionally, C-H vibrational strains in cellulose are evident at 899 cm^{-1} [13]. A band at 1466 cm^{-1} is attributed to the stretching vibrations of the C-N group confirming the successful modification of the cellulosic material [14]. The overall shape and position of the bands remained largely unchanged after dye adsorption. However, a slight shoulder at 3300 cm^{-1} and increased intensity of the broad band around 3440 cm^{-1} , attributed to hydrogen-bonded -OH groups, was noted. The peaks at 2852 cm^{-1} and 1650 cm^{-1} , corresponding to C-H and C=O stretching, shifted to 2886 cm^{-1} and 1644 cm^{-1} , respectively, after RB adsorption. Additionally, the C-O stretching peak at 1064 cm^{-1} shifted slightly to 1061 cm^{-1} after RB removal. The peak at 1115 cm^{-1} due to OH-group in cellulose [15], shifted to 1111 cm^{-1} .

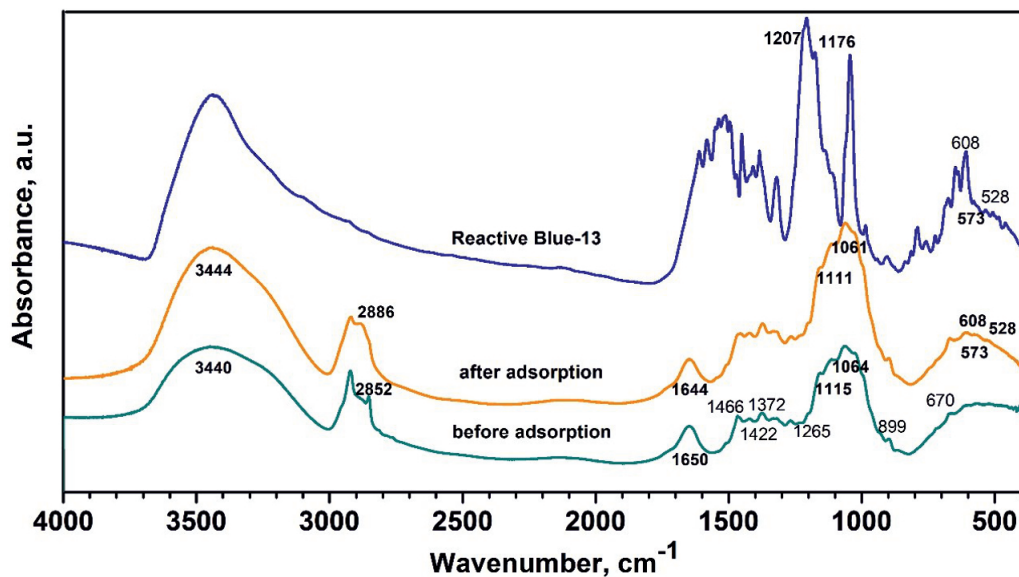


Fig. 3. FTIR spectra of cellulosic material before and after RB adsorption

Bands at 608, 573 and 528 cm^{-1} which appeared after RB adsorption, are attributed to C–Cl functional groups of the dye. The sharp peaks at 1207 cm^{-1} and 1176 cm^{-1} , corresponding to S=O stretching in RB, do not appear in the spectrum after dye removal. FTIR analysis suggests that interactions occurred between the OH, C–O, and C=O groups of the cellulosic material and the $\text{–SO}_3\text{H}$ groups of the dye. This finding aligns with CHOWDHURY's study [16].

Conclusions. In this study, the efficiency of a cationized rice husk-derived cellulosic adsorbent for removing Reactive Blue 13 dye from water was investigated. The highest removal efficiency occurred at pH 2, with rapid adsorption reaching equilibrium within 60 min, indicating a strong affinity for the dye. The equilibrium data fit well with the Langmuir isotherm, suggesting a monolayer adsorption process. Kinetic analysis showed that the adsorption followed a pseudo-second-order model, while thermodynamic parameters indicated an endothermic reaction, with ΔH^0 of 18.50 kJ mol^{-1} and ΔS^0 of $95.44\text{ J mol}^{-1}\text{K}^{-1}$. The adsorbent's maximum capacity was 53.16 mg g^{-1} . Additionally, a 1 M NaOH solution effectively regenerated the material, supporting its reuse potential. These findings demonstrate that renewable agricultural waste can be converted into a value-added product with promising applications in environmental protection against pollutants like Reactive Blue 13.

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