

# Decolorization of Wastewater from Pulp and Paper Industry by Adsorption on Talc



This work is licensed under a  
Creative Commons Attribution 4.0  
International License

N. Šoltýsová,\* J. Jurík, R. Zakhar, and J. Derco

Department of Environmental Engineering,  
Faculty of Chemical and Food Technology,  
Slovak University of Technology,  
Radlinského 9, 812 37 Bratislava, Slovakia

doi: <https://doi.org/10.15255/CABEQ.2024.2297>

Original scientific paper  
Received: March 12, 2024  
Accepted: May 23, 2024

This study focuses on the elimination of residual dyes from industrial wastewater using talc as an adsorbent. Talc is an easily available, ecological, and inexpensive adsorbent. The adsorption process was tested on two model dye samples (Ecozol Blue LR Liquid and Cartasol Yellow 3GF Direct Yellow 132), and two samples of real wastewater from the pulp and paper industry (PM and TP). Kinetic studies revealed that the adsorption of Ecozol Blue LR Liquid followed pseudo-second-order kinetics, while the other tested samples followed pseudo-first-order kinetics. Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherm models were also evaluated. The Langmuir isotherm model best fitted the experimental data for the adsorption of model dye solutions and wastewater sample TP onto talc. For wastewater sample PM, the Dubinin-Radushkevich isotherm model provided the best fit to the experimental data. The results of the adsorption isotherms indicated that the adsorption of all tested systems was favorable and primarily involved physical adsorption. The adsorption efficiency for the model solutions exceeded 90 %. For real wastewater samples, the monitored adsorption efficiency in the COD pollution indicator was less efficient, ranging from 43 to 51 %. The lower efficiency of COD may have resulted from the adsorption of residual dyes with lower specific COD values before the adsorption of other organics.

## Keywords

adsorption, azo dyes, cationic talc, pulp and paper industry, wastewater

## Introduction

Humans are inherently artistic and have strong reactions to different styles and colors. Colors can also signal various things, such as dangers, alerts, notifications, or differentiate objects by appearance, and they can simply serve for our amusement. The materials used to make objects visually distinct are known as colorants. These are widely used in various industries, such as the production of clothes, paints, plastics, photographs, prints, and ceramics. Most people are familiar with colorants known as dyes. Dyes are soluble, colored organic compounds applied from a water solution onto textiles, creating robust bonds with polymer molecules of the fiber.<sup>1</sup> The widespread use of dyes in industry leads to their presence in the environment.<sup>2</sup> For example, residues of dyes in wastewater that are subsequently discharged into water bodies can negatively impact the aquatic ecosystem. These impacts include unnatural discoloration of the water, problems related to oxygen transfer, absorption, and reflection of sunlight entering the water, and the toxicity of some

dyes. Due to the absorption of radiation by dyes, the photosynthetic activity of algae is reduced, which consequently affects the entire food chain of the aquatic community.<sup>3,4</sup>

Azo dyes are the most widely used in industry. Residual azo dyes in the environment can bioaccumulate in aquatic animals, causing toxicity and mutagenicity. Anaerobic reduction of azo dyes produces amines, which have proven carcinogenic effects associated with sarcomas of the spleen, bladder cancer, and hepatocarcinoma, causing anomalies in experimental animals.<sup>4</sup>

The removal of unwanted substances and dyes, specifically in our case, requires the application of water treatment methods. One method is adsorption, which necessitates a material with a large surface area where pollutants can be sorbed from the surrounding medium. The final stage of this process takes place on the adsorbent, where the adsorbate adheres to suitable sites. The efficacy of this process depends not only on the physicochemical conditions but also on the characteristics of the adsorbent. The ideal material must be non-toxic, environmentally friendly, inexpensive, easy to handle, and as efficient as possible.<sup>5</sup> Activated carbon

\*Corresponding author: email: [nikola.soltysova@stuba.sk](mailto:nikola.soltysova@stuba.sk)

is the most well known and widely used adsorbent due to its high adsorption capacity. However, commercially available activated carbon-based adsorbents are relatively expensive. Consequently, many researchers are seeking more affordable and effective alternatives for dye removal. Clay minerals could serve as alternative adsorbents due to their easy availability, low cost, non-toxicity, large surface area, and ion exchange potential compared to activated carbon.<sup>6–8</sup> Grafia *et al.* suggested talc as an inexpensive mineral for wastewater treatment. They compared the adsorption of methylene blue on sepiolite (a highly effective adsorbent) and talc, demonstrating that talc is a good dye adsorbent.<sup>9</sup> The effective adsorption of methylene blue from an aqueous solution onto talc has also been confirmed in other studies.<sup>10,11</sup> A study by Sonba and Ridha compared modified kaolin clay and talc as adsorbents for removing an industrially important dye, Eriochrome Black T. They reported that talc was more effective than modified kaolin in removing Eriochrome Black T.<sup>12</sup> It is important to note that both methylene blue and Eriochrome Black T are cationic dyes.<sup>9–12</sup>

Rahman *et al.* compared three clay adsorbents – sepiolite, kaolin, and synthetic talc – for the removal of an anionic dye (Reactive Yellow 138:1). Talcum powder exhibited higher adsorption efficiency than the other two adsorbents, primarily removing dyes through physical adsorption. It is important to note that the anionic nature of the dye allows talc to remove it by adsorption and anion exchange.<sup>13</sup>

In the available literature on the adsorption of dyes using talc, the focus has predominantly been on dyes used in the textile industry.<sup>5–13</sup> The novelty of this paper lies in its focus on the pulp and paper industry, where talc is primarily used to control issues related to dissolved and colloidal material in papermaking.<sup>14,15</sup> This makes talcum powder a suitable choice for adsorption in the decolorization of wastewater, as the pulp and paper industry typically has a reserve of talcum powder.

In our study, we focused on the potential of using cationic talc Mistron<sup>®</sup>75-6 KA to adsorb anionic dyes (Ecozol Blue LR Liquid and Cartasol Yellow 3GF Liquid) used in the pulp and paper industry. Since there is no published literature on these specific dyes, we conducted basic kinetics studies (pseudo-first and pseudo-second order) and applied adsorption isotherm models (Langmuir, Freundlich, Dubinin-Radushkevich). The aim was to determine the nature of the adsorption process and the values of the constants for the applied isotherm models, necessary for designing an adsorption process as a potential pretreatment option before the biological stage of wastewater treatment.

## Materials and methods

### Analytical methods

Given that the samples were colored, we used spectrophotometric methods to determine the dye concentrations after the adsorption process. We analyzed the absorption spectrum in the visible region for individual samples using a benchtop DR 6000 Hach Lange spectrophotometer. The DR 6000 covers the visible spectrum in the wavelength range of 320 to 1100 nm using a halogen lamp, while a deuterium lamp emits light in the ultraviolet spectrum in the wavelength range of 190 to 360 nm.<sup>16</sup> Additionally, the organic matter content was determined by measuring the chemical oxygen demand (COD) using a Hach Lange LCK514 cuvette test.

### Model and real wastewater samples

In this case study, we focused on two problematic dyes used in the pulp and paper industry: Ecozol Blue LR Liquid (Waterside Colours Ltd., UK) and Cartasol Yellow 3GF Liquid (Archroma, Switzerland). Ecozol Blue LR Liquid is a mid-shade blue dye classified as an anionic dye. According to the information data sheet, it is a double azo copper complex dye.<sup>17</sup> The structural formula of this dye is not available in the literature. Cartasol Yellow 3GF Liquid has a yellow hue and is also an anionic double azo dye.<sup>18</sup> The structure of Cartasol Yellow 3GF Liquid is shown in Fig. 1. Both dyes are classified as direct dyes and are used in both the paper and textile industries. Direct dyes are characterized by an azo group and are sodium salts or metal compounds (such as chromium or copper).<sup>19</sup> Basic information about these dyes is summarized in Table 1.

Table 1 – Basic information about the dyes<sup>17,18</sup>

Dye	Ecozol Blue LR Liquid	Cartasol Yellow 3GF Liquid
Generic name	Direct blue 290	Direct yellow 132
CAS number	110444-91-2	61968-26-1
Classification based on	use	direct dye
	structure	azo dye

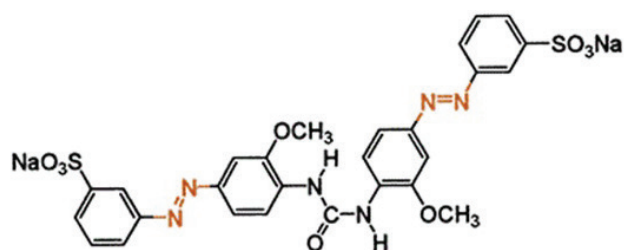


Fig. 1 – Chemical structure Cartasol Yellow 3GF (Direct yellow 132)<sup>18</sup>

For the adsorption experiments, working solutions of individual dyes were prepared with a mass concentration of 200 mg L<sup>-1</sup>.

Two real wastewater samples from the pulp and paper industry were also available. Specifically, one effluent was from the outlet of a paper mill (PM), and the second from the inlet of the first stage of a wastewater treatment plant (TP). The PM sample mainly contained residual dyes, with a chemical oxygen demand (COD) of 1 421 mg L<sup>-1</sup>. The TP sample was a mixed wastewater from a paper mill, chemical recovery, pulp mill, pulp bleaching, and vapor condensates, also including sewage from the industry's workers. The COD value of TP sample was 1 085 mg L<sup>-1</sup>. The pH value of both wastewater samples was approximately 7.5.

### Adsorbent Mistron®75-6 KA

We used the adsorbent Mistron®75-6 KA (Imerys Performance Minerals, Austria) to remove the dyes from the working solutions and wastewater samples. This type of cationic talc is used in the pulp and paper industry to control pitch and stickiness in papermaking. It is highly effective in reducing anionic waste, is soft, hydrophilic, economical, and has a high affinity for organic substances. This adsorbent has an average particle diameter of 3.5 μm, with only 30 % of the particles smaller than 2 μm. The specific density and bulk density were 2.78 g m<sup>-3</sup> and 0.4 g m<sup>-3</sup>, respectively. According to the product data sheet of this adsorbent, its specific surface area is 8.5 m<sup>2</sup> g<sup>-1</sup>.<sup>20</sup> In general, talc is defined as powdered native hydrous magnesium silicate, which can sometimes contain small portions of aluminum silicate. The chemical composition of talc generally consists of MgO 31.7 %; SiO<sub>2</sub> 63.5 % and H<sub>2</sub>O 4.8 %, with a formula Mg<sub>3</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub>.<sup>21</sup>

### Adsorption experiment

A batch adsorption experiment was carried out in this study. The adsorption process took place on an orbital shaker RSLAB-7PRO (Kvant s.r.o.; Slovakia), at 150 rpm to achieve the greatest possible adsorption efficiency. For the kinetic study experiments, 100 mL of sample and 1 gram of adsorbent were added into 5 to 8 flasks. The initial dye concentration was 200 mg L<sup>-1</sup>. For wastewater, the initial COD value was the same as the COD of the original sample. The adsorption time varied between 0 and 60 minutes. For the experiments to obtain adsorption isotherm data, 100 mL of sample and 1 gram of adsorbent were also used. The initial dye concentration in these experiments varied between 50 and 400 mg L<sup>-1</sup>, and the initial COD value of the wastewater ranged from 150 to 1 421 mg L<sup>-1</sup> (or 1 085 mg L<sup>-1</sup>). All adsorption experiments were

conducted at a constant pH (neutral) and a temperature of 20 °C.

After adsorption, the suspension was processed by centrifugation for 5 minutes at 2 900 rpm. The absorbance of the supernatant was measured at the working wavelength depending on the sample used, allowing us to calculate the concentration after the adsorption process.

The adsorption process was evaluated by calculating the amount of adsorbate (adsorption capacity) in equilibrium and removal efficiency (adsorption efficiency):<sup>22</sup>

$$q = \left( \frac{C_0 - C_e}{m} \right) \cdot V \quad (1)$$

$$\text{removal efficiency} = \frac{C_0 - C_e}{C_0} \cdot 100 \% \quad (2)$$

where  $q$  (kg kg<sup>-1</sup>) is the adsorption capacity,  $m$  (kg) is mass of adsorbent material,  $V$  (m<sup>3</sup>) is volume of sample, and  $C_0$ ,  $C_e$  (kg m<sup>-3</sup>) is concentration of sample at the start of experiments and equilibrium concentration (final concentration).<sup>22</sup>

### Experimental data processing

#### Adsorption kinetics

The kinetics of the adsorption process was described by the pseudo-first order (Eq. 3) and pseudo-second order kinetics (Eq. 4). These kinetic equations are commonly used to describe adsorption data obtained under non-equilibrium conditions.<sup>22</sup>

$$q_t = q_e (1 - e^{-k_1 t}) \quad (3)$$

$$q_t = q_e \frac{k_2 q_e t}{1 + k_2 q_e t} \quad (4)$$

where  $q_e$ ,  $q_t$  (g kg<sup>-1</sup>) is the adsorption capacity in equilibrium and adsorption capacity at time  $t$  (h),  $k_1$  (h<sup>-1</sup>),  $k_2$  (kg g<sup>-1</sup> h<sup>-1</sup>) are the pseudo-first and pseudo-second order rate constants.<sup>22</sup> The pseudo-first-order kinetic equation assumes that the adsorption site occupancy rate is proportional to the number of vacancies, while the pseudo-second-order kinetic model assumes that the adsorption site occupancy rate is proportional to the square of the vacancies.<sup>23,24</sup>

#### Adsorption isotherms

Adsorption isotherms were used to describe the adsorption process. They show the dependence of the adsorption capacity on pressure or the adsorbate concentration under equilibrium conditions at a constant temperature. In this study, the Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherm models were used to describe this dependence.

The Langmuir isotherm assumes monolayer adsorption onto a surface with a finite number of uniform strategy adsorption sites, and no adsorbate transmigration on the plane surface. Once a site is filled, it cannot be used for further sorption. This suggests that the surface has reached a saturation point at which its maximum adsorption is achieved.<sup>25–27</sup> The Langmuir isotherm is expressed by the following equation (Eq. 5):<sup>27</sup>

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (5)$$

where  $q_{\max}$  (g kg<sup>-1</sup>) is the maximum adsorbent capacity, and  $K_L$  (m<sup>3</sup> g<sup>-1</sup>) is the Langmuir constant.<sup>27</sup> The equilibrium parameter, or separation factor  $R_L$ , is an important component of the Langmuir isotherm model. It is used to determine if adsorption is favorable or unfavorable and is dependent on the Langmuir constant  $K_L$ :<sup>27</sup>

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

If the  $R_L$  value is less than 1, adsorption is considered favorable; if it is close to 0, it is irreversible; if it equals 1, the adsorption isotherm is nonlinear, and if it is greater than 1, adsorption is unfavorable.<sup>24,28,29</sup>

The Freundlich isotherm describes an empirical model for multilayer adsorption at heterogeneous sites. It assumes that the adsorption heat distribution and the affinity for non-uniform surfaces are not uniform.<sup>24,30</sup> The mathematical model is expressed as follows:<sup>31</sup>

$$q_e = K_F C_e^{1/n} \quad (7)$$

where  $K_F$  (g<sup>(1-1/n)</sup> kg<sup>-1</sup> m<sup>-3</sup>) and  $n$  are empirical constants.<sup>31</sup> The  $n$  value indicates the degree of nonlinearity between solution concentration and adsorption, as follows: if  $n$  equals 1, adsorption is linear; if  $n$  is less than 1, adsorption is a chemical process; if  $n$  is more than 1, adsorption is a physical process. The definition of surface heterogeneity or adsorption intensity is  $1/n$ . It is considered that adsorption is favorable when  $0 < 1/n < 1$ . When  $1/n > 1$ , unfavorable adsorption takes place and becomes irreversible at  $1/n = 1$ .<sup>30–32</sup>

The empirical Dubinin-Radushkevich isothermal adsorption model is commonly used to express the adsorption mechanism with Gaussian energy distribution on heterogeneous surfaces. It is usually applied to differentiate between physical and chemical adsorption.<sup>33,34</sup> The mathematical expression of the Dubinin-Radushkevich isotherm is as follows:<sup>35</sup>

$$q_e = q_{\max} \exp(-\beta \varepsilon^2) \quad (8)$$

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (9)$$

$$E = \frac{1}{\sqrt{2\beta}} \quad (10)$$

where  $\varepsilon$  is Polanyi potential (kJ mol<sup>-1</sup>),  $\beta$  (mol<sup>2</sup> kJ<sup>2</sup>) is Dubinin-Radushkevich constant,  $R$  is gas constant (8.31 J mol<sup>-1</sup> K<sup>-1</sup>),  $T$  (K) is thermodynamic temperature, and  $E$  (kJ mol<sup>-1</sup>) is mean adsorption energy.<sup>35</sup> The  $E$  value resulting from the Dubinin-Radushkevich isotherm can determine whether a physisorption or chemisorption process has occurred. Physisorption processes have adsorption energies in the range of 1–8 kJ mol<sup>-1</sup>, while chemisorption processes have an adsorption energy greater than 8 kJ mol<sup>-1</sup>.<sup>34–37</sup>

The values of the constants of the adsorption kinetics and adsorption isotherms were determined using the nonlinear regression analysis technique in Origin Software version No. 8.50013.

## Results and discussion

### Absorption spectrum

The absorption spectrum in the visible region of 380–700 nm was measured for each sample to determine the working wavelength. For a diluted Ecozol Blue LR Liquid dye solution, the maximum absorbance was at wavelength 591 nm. For the Cartasol Yellow 3GF dye solution, the maximum wavelength was found at 438 nm. Spectrophotometric analysis of the real wastewater samples determined the working wavelength for the PM sample at 396 nm and for the TP sample at 398 nm. After determining the working wavelength, we prepared sets of solutions with different concentrations for the individual dyes and wastewater samples to construct calibration curves, which were used to determine the concentration of dyes after the adsorption process.

### Adsorption process

#### Adsorption kinetics

In the first step of the adsorption process, it was necessary to determine the equilibrium time - the point at which the adsorption capacity stabilizes. Time dependencies of adsorption capacity were constructed for individual samples using pseudo-first and pseudo-second order kinetic equations. Based on the value of the kinetic constant  $q_e$  of the more suitable kinetic order, the equilibrium time was determined. The time profile of adsorption capacity for dye solution is shown in Fig. 2, and for the real wastewater sample in Fig. 3. For all samples, we observed a rapid increase in adsorption capacity in the first 5–10 minutes, likely due to the abundant availability of active sites on the surface



of the adsorbent.<sup>38</sup> The values of the constants of the used kinetic equations are listed in Table 2. Based on the statistical characteristics, the pseudo-second-order kinetic model was more suitable for the Ecozol Blue LR Liquid sample. The equilibrium adsorption capacity constant ( $q_e$ ) from pseudo-second-order kinetics was  $21.0 \text{ g kg}^{-1}$ . However, the adsorption capacity began to stabilize after 17.5 minutes, with experimental values of approximately  $19 \text{ g kg}^{-1}$ . Therefore, the equilibrium time for the adsorption of Ecozol Blue LR Liquid was found to be 17.5 minutes.

For the other samples, the pseudo-first-order kinetics was more suitable. For the Cartasol Yellow 3GF sample, the value of  $q_e$  was  $36.2 \text{ g kg}^{-1}$ , with an equilibrium time of 20 minutes on the Mistron<sup>®</sup>75-6 KA adsorbent. For the PM sample, the value of the  $q_e$  constant from pseudo-first-order kinetics was  $64.4 \text{ g kg}^{-1}$ . The experimental values of adsorption capacity reached approximately this value in 30 minutes, after which the experimental values of adsorption capacity remained relatively unchanged. Thus, the equilibrium time for the PM sample was determined to be 30 minutes. For the TP sample, the experimental values of the adsorption capacity began to stabilize 10 minutes earlier compared to the PM sample. The value of the  $q_e$  constant from the better-fitting kinetics order was  $54.2 \text{ g kg}^{-1}$ , which also corresponded to the experimental values at the time of stabilization, as shown in Fig. 3. Thus, the equilibrium time for the TP sample was determined to be 20 minutes.

**Adsorption isotherms**

Additional adsorption experiments were conducted under equilibrium conditions for all samples to evaluate the adsorption isotherm. These experi-

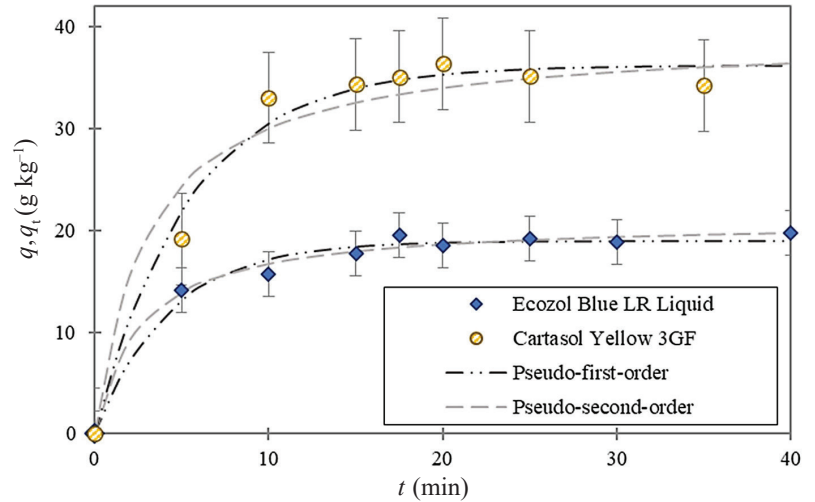


Fig. 2 – Time profile of adsorption capacity during adsorption of dye solutions

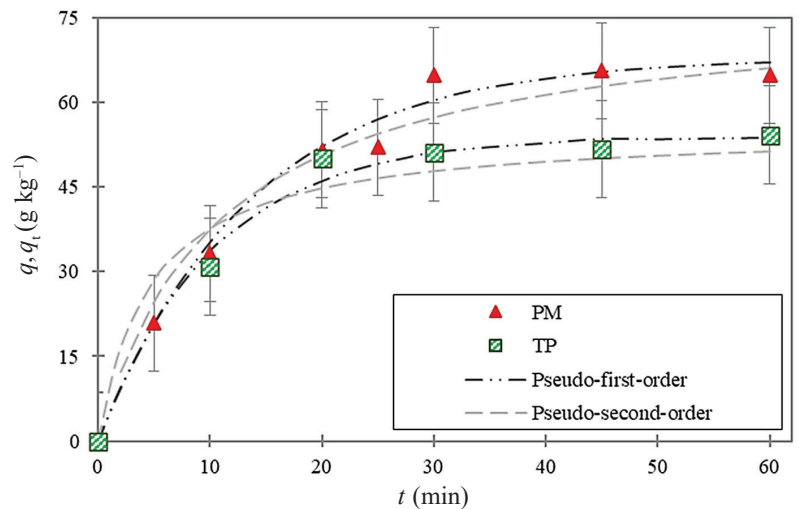


Fig. 3 – Time profile of adsorption capacity during adsorption of wastewater samples

ments were conducted at the established equilibrium times. The values of the empirical constants of the adsorption isotherms were determined using nonlinear regression and are listed in Tables 3, 4, and 5. Based on the parameters of individual adsorption isotherms, we can assess whether the adsorption process is reversible or irreversible, favorable or unfavorable, and whether it is chemisorption or physisorption.<sup>24,28,29</sup> The graphic representations

Table 2 – Kinetic and statistical parameters of the applied kinetic models

	Pseudo-first-order kinetics				Pseudo-second-order kinetics			
	$q_{max}$ ( $\text{g kg}^{-1}$ )	$k_1$ ( $\text{h}^{-1}$ )	<i>SSE</i>	$R^2$	$q_{max}$ ( $\text{g kg}^{-1}$ )	$k_2$ ( $\text{kg g}^{-1} \text{h}^{-1}$ )	<i>SSE</i>	$R^2$
Ecozol Blue LR Liquid	19.1	14.0	5.08	0.984	21.0	1.10	2.88	0.991
Cartasol Yellow 3GF	36.2	11.1	5.66	0.983	39.2	0.50	15.66	0.949
PM	64.4	4.4	29.30	0.992	75.0	0.07	48.39	0.934
TP	54.2	5.7	27.43	0.988	55.0	0.24	94.19	0.946

Table 3 – Parameters and statistical values of the Langmuir isotherm

	$q_{\max}$ (g kg <sup>-1</sup> )	$K_L$ (L mg <sup>-1</sup> )	$C_0$ (mg L <sup>-1</sup> )	$R_L$	SSE	$R^2$
Ecozol Blue LR Liquid	19.8	0.58	200.0	0.01	1.80	0.994
Cartasol Yellow 3GF	68.6	0.08	200.0	0.05	48.72	0.979
PM	85.1	0.02	1 421	0.03	422.38	0.926
TP	31.0	0.01	1 085	0.08	29.89	0.955

Table 4 – Parameters and statistical values of the Freundlich isotherm

	$K_F$ g <sup>(1-1/n)</sup> kg <sup>-1</sup> m <sup>-3</sup>	$n$	1/n	SSE	$R^2$
Ecozol Blue LR Liquid	17.5	74.0	0.01	7.58	0.955
Cartasol Yellow 3GF	20.0	4.05	0.25	223.92	0.905
PM	10.2	2.94	0.34	238.48	0.984
TP	7.69	5.00	0.20	51.63	0.922

of the adsorption isotherms are shown in Figs. 4 – 7.

From the  $K_L$  constants of the Langmuir isotherm for each sample, the separation factor  $R_L$  was calculated according to the Eq. 5. The values of the calculated separation factors are given in Table 3. For each examined sample in the tested concentration range, the  $R_L$  value was less than 1, indicating that the adsorptions of the individual samples on Mistron<sup>®</sup>75-6 KA adsorbent were favorable. Also, the  $R_L$  values being close to zero suggest that this process is irreversible.<sup>24,28–29</sup>

From the Freundlich isotherm, it is possible to determine whether the adsorption is chemical or physical. Additionally, the favorability and irreversibility of the adsorption process can be confirmed or refuted from the reciprocal value of the empirical constant  $n$ . For each sample, the value of the empirical constant  $n$  was greater than 1 (Table 4), indicating that the adsorptions were physical. Since the values are greater than 1, the reciprocal would be less than 1, confirming the favorability of the adsorption from the Langmuir isotherm, indicating that the adsorptions are reversible.<sup>30–32</sup>

The value of adsorption energy  $E$  resulting from the Dubinin-Radushkevich isotherm can determine whether a physisorption or chemisorption process

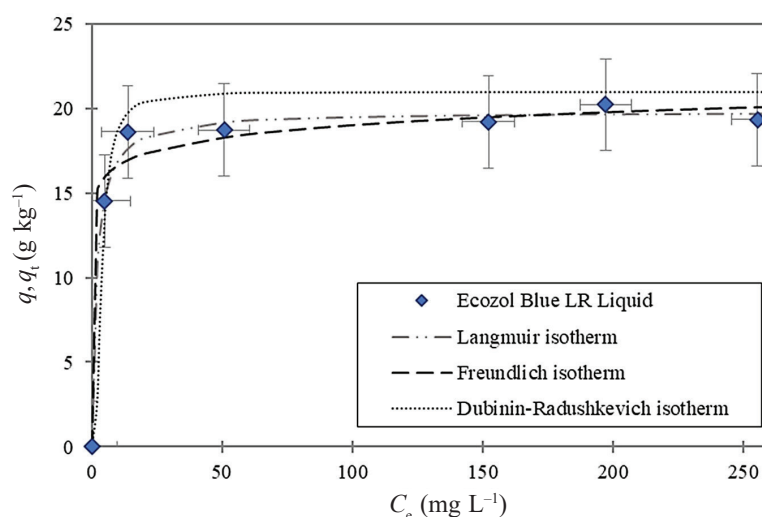


Fig. 4 – Adsorption isotherms for dye solutions of Ecozol Blue LR Liquid

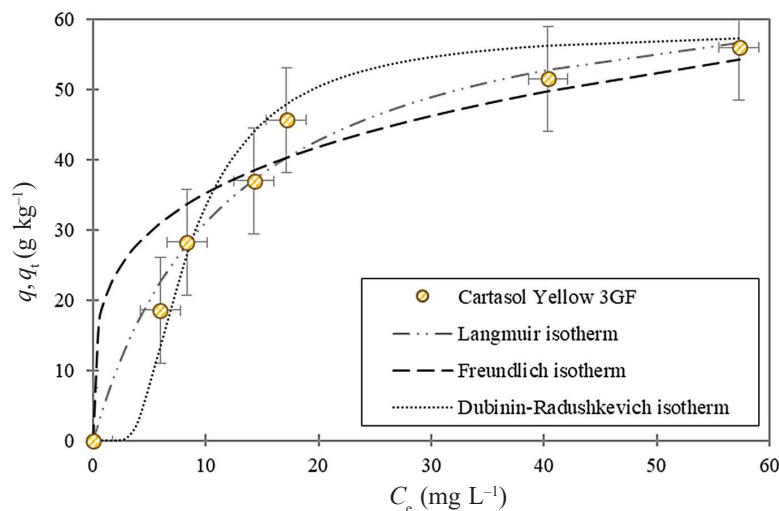


Fig. 5 – Adsorption isotherms for dye solutions of Cartasol Yellow 3GF

has occurred. In Table 5, we can see the parameters resulting from the Dubinin-Radushkevich isotherm. For each sample, the adsorption energy value is less than 8 kJ mol<sup>-1</sup>, indicating physisorption. This finding aligns with the Freundlich isotherm, confirming that the adsorption of all tested samples on the Mistron<sup>®</sup>75-6 KA adsorbent was physical.<sup>34–37</sup>

Based on the  $R^2$  values of the applied isotherm models for individual adsorption systems (Table 6), the best-fitted isotherm model was evaluated. The Langmuir isotherm model provided the best fit to the experimental data for the adsorption of model dye solutions onto talc. The  $R^2$  value of the Langmuir isotherm for the Ecozol Blue LR Liquid sample was 0.994, and for Cartasol Yellow 3GF, it was 0.979. The  $R^2$  values of the other isotherm models for these model dye solutions was less than 0.960. The Langmuir isotherm model also provided the best fit to the experimental data for the TP sample, with a calculated  $R^2$  value of 0.955. For the Freundlich and Dubinin-Radushkevich isotherm models,  $R^2$  values were 0.922 and 0.862, respectively. The Dubinin-Radushkevich isotherm model was the best fit for the PM wastewater sample, with an  $R^2$  value of 0.984, while the Langmuir and Freundlich isotherm values were 0.926 and 0.958, respectively.

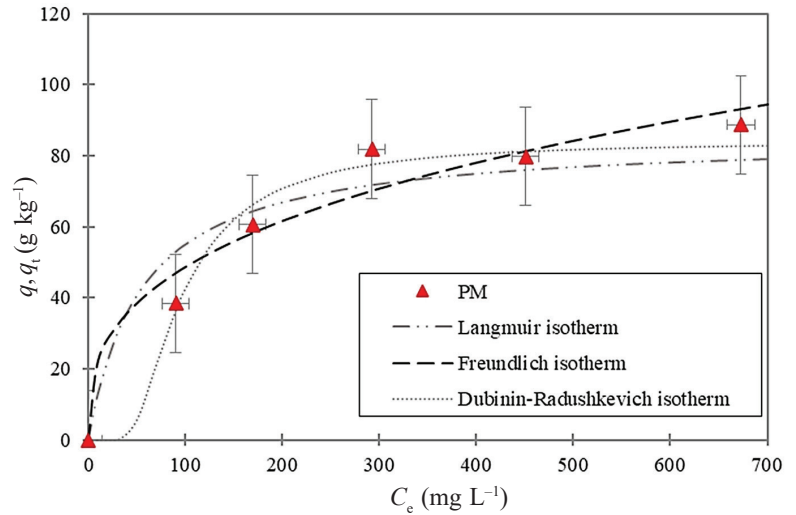


Fig. 6 – Adsorption isotherms for PM wastewater sample

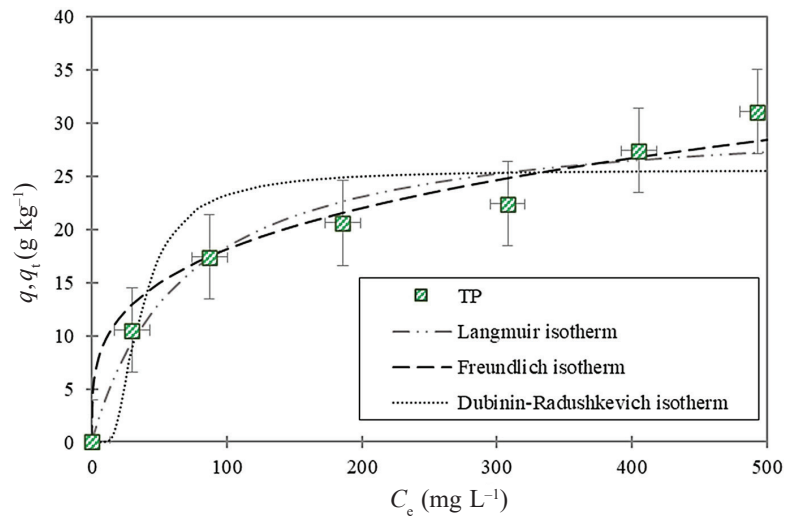


Fig. 7 – Adsorption isotherms for TP wastewater sample

Table 5 – Parameters and statistical values of the Dubinin-Radushkevich isotherm

	$q_{max}$ (g kg <sup>-1</sup> )	$\beta$ (mol <sup>2</sup> kJ <sup>2</sup> )	$E$ (kJ mol <sup>-1</sup> )	SSE	$R^2$
Ecozol Blue LR Liquid	21.0	$2.0 \cdot 10^{-6}$	0.49	12.89	0.958
Cartasol Yellow 3GF	58.4	$1.0 \cdot 10^{-5}$	0.22	84.69	0.954
PM	83.9	$1.2 \cdot 10^{-3}$	0.02	91.96	0.984
TP	25.6	$1.6 \cdot 10^{-4}$	0.06	91.53	0.862

Table 6 – Comparison of the  $R^2$  values of the applied isotherm models

	Langmuir isotherm	Freundlich isotherm	Dubinin-Radushkevich isotherm
Ecozol Blue LR Liquid	0.994	0.955	0.958
Cartasol Yellow 3GF	0.979	0.905	0.954
PM	0.926	0.958	0.984
TP	0.955	0.922	0.862

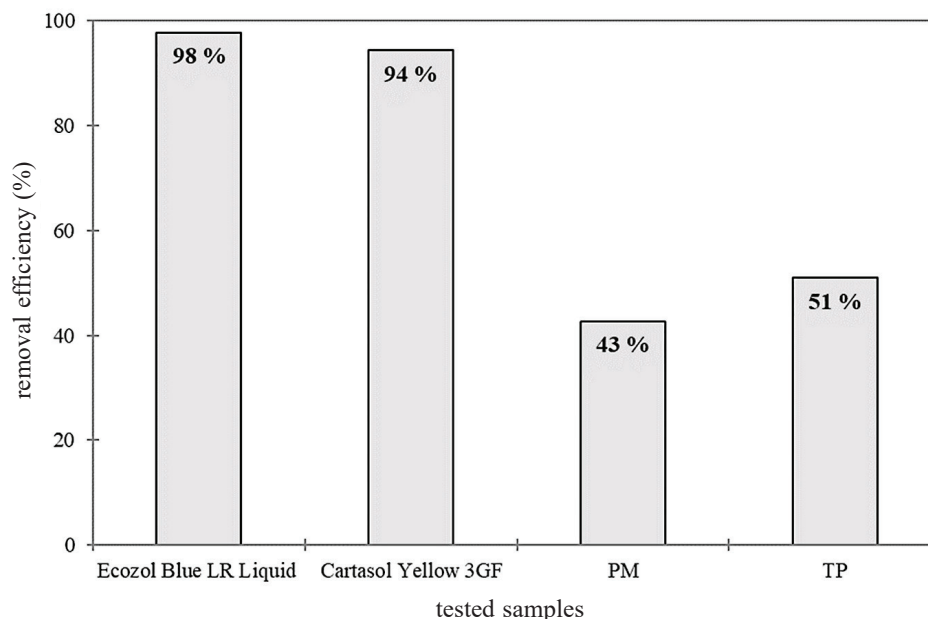


Fig. 8 – Adsorption efficiency

#### Adsorption efficiency

In general, the adsorption efficiency was high under equilibrium conditions, exceeding 90 % for dye solutions with a concentration of  $200 \text{ mg L}^{-1}$ . Specifically, the adsorption efficiency was 98 % for Ecozol Blue LR Liquid and 94 % for Cartasol Yellow 3GF. A lower adsorption efficiency was observed for the wastewater samples. However, a decrease in COD was recorded for these samples to evaluate whether talc as an adsorbent is also effective in removing organic pollutants. The removal efficiencies are shown in Fig. 8. The COD removal efficiency was 43 % for the sample from the paper mill (PM). The lower COD removal efficiency for this sample was likely due to the preferential adsorption of residual dyes over other organic substances. A higher COD removal efficiency (51 %) was observed for the wastewater sample from the entrance to the wastewater treatment plant (TP) on the premises of the pulp and paper industry. Residual dyes in wastewater can have an adverse effect on the biological stage of wastewater treatment or may not be removed in the activated sludge process, leading to their release into the environment.<sup>39</sup> Adsorption on the tested talc could therefore be a suitable method for pre-treating wastewater before it enters the biological stage of the WWTP. The results indicate that this adsorbent is effective in the elimination of dyes used in the given industry.

The tested adsorption process has several advantages: cationic talc is an easily available, ecological, and inexpensive adsorbent. At the same time, it is assumed that anionic pollutants, such as dyes used in the pulp and paper industry, are preferentially adsorbed onto talc. However, the main dis-

advantage is the form of the adsorbent. This study used powdered talc, which presents challenges in solid–liquid separation, transmission loss, and poor permeability due to its small particle size and difficult settling characteristics.<sup>40,41</sup>

#### Conclusion

This study investigated the adsorption of industrial dyes using a cationic type of talc for the removal of anionic dyes. This adsorbent was tested on both model wastewater containing the studied dyes and on real wastewater from the pulp and paper industry. The results of this study indicate that talc is applicable for the pretreatment of wastewater in this industry. Kinetic studies revealed that the adsorption of Ecozol Blue LR Liquid followed pseudo-second-order kinetics, while the other tested samples followed pseudo-first-order kinetics. The adsorption isotherms indicated that the adsorption processes for all tested systems were favorable and involved physical adsorption. The adsorption efficiency for the model solutions exceeded 90 %. For real wastewater samples, the adsorption efficiency, as measured by the COD pollution indicator, was lower, ranging from 43 to 51 %. Future work should focus on the design, modeling, and implementation of the adsorption process as a pretreatment step before the biological stage of the wastewater treatment plant. The design of the adsorption process should be specifically tailored to the pulp and paper industry, from which the wastewater samples were obtained. The results of this study provide a solid foundation for the practical design of the adsorption process.



## References

1. Mahapatra N. N., Textile Dyes. Woodhead Publishing India PVT LTD, New Dehli, 2016.
2. Rahman, A., Urabe, T., Kishimoto, N., Color removal of reactive procion dyes by clay adsorbents, *Procedia Environ. Sci.* **17** (2013) 270.  
doi: <https://doi.org/10.1016/j.proenv.2013.02.038>
3. Gürses, A., Açıkyıldız, M., Güneş, K., Sadi Gürses, M., Dyes and Pigments, Springer, Cham, 2016, 162 p.
4. Malik, A., Grohmann, E., Environmental protection strategies for sustainable development, Springer, Dordrecht, The Netherlands (2012) 946 p.
5. Chaari, I., Moussi, B., Jamoussi, F., Interactions of the dye, C.I. direct orange 34 with natural clay, *J. Alloys Compd.* **647** (2015) 720.  
doi: <https://doi.org/10.1016/j.jallcom.2015.06.142>
6. Adeyemo, A. A., Adeoye, I. O., Bello, O. S., Adsorption of dyes using different types of clay: A review, *Appl. Water Sci.* **7**(2) (2015) 543.  
doi: <https://doi.org/10.1007/s13201-015-0322-y>
7. Uddin, M. K., A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade, *Chem. Eng. J.* **308** (2017) 438.  
doi: <https://doi.org/10.1016/j.cej.2016.09.029>
8. Arabmofrad, S., Bagheri, M., Rajabi, H., Jafari, S. M., 4 – Nanoadsorbents and nanoporous materials for the food industry, *Appl. Approach* (2020) 107.  
doi: <https://doi.org/10.1016/B978-0-12-815866-1.00004-2>
9. Grafia, A. L., Castillo, L. A., Barbosa, S. E., Use of talc as low-cost clarifier for wastewater, *Water Sci. Technol.* **69**(3) (2014) 640.  
doi: <https://doi.org/10.2166/wst.2013.755>
10. Li, S. F., Yang, S. C., Zhao, S. L., Li, P., Zhang, J. H., Microwave and acid modified talc as adsorbents of methylene blue in aqueous solution, *J. Serb. Chem. Soc.* **80**(4) (2015) 563.  
doi: <https://doi.org/10.2298/JSC140718116L>
11. Bilgiç, M., Şimşek, S., Şenol, Z. M., Removal of methylene blue dye from aqueous solution using pure talc and polyacrylamide–talc composite: Isotherms, kinetic and thermodynamic studies, *Polym. Bull.* **80**(10) (2023) 11049.  
doi: <https://doi.org/10.1007/s00289-022-04602-7>
12. Sonba, H. J., Ridha, S. H., Thermodynamics of adsorption of eriochrome black-t dye from aqueous media on each modified kaolin clay and talc, *Acta Chim. Pharm. Indica* **4**(2) (2014) 111.
13. Rahman, A., Kishimoto, N., Urabe, T., Adsorption characteristics of clay adsorbents–sepiolite, kaolin and synthetic talc—for removal of Reactive Yellow 138:1, *Water Environ. J.* **29**(3) (2015) 375.  
doi: <https://doi.org/10.1111/wej.12131>
14. Guéra, N., Schoelkopf, J., Gane, P. A., Rauatmaa, I., Comparing colloidal pitch adsorption on different talcs, *Nordic Pulp Pap. Res. J.* **20**(2) (2005) 156.  
doi: <https://doi.org/10.3183/NPPRJ-2005-20-02-p156-163>
15. Tijero, A., Monte, M. C., Blanco, A., Tijero, J., Use of talc to control problems associated with dissolved and colloidal material in papermaking, *Tappi J.* **11**(2) (2012) 51.  
doi: <https://doi.org/10.32964/TJ11.2.43>
16. DR 6000 USER MANUAL. Edition 4. 2018. Hach Company/Hach Lange GmbH, Germany. DOC022.52.90367
17. ECOZOL™ Blue LR Liquid. Product data sheet. 2017. Waterside Colours Ltd., United Kingdom.
18. Caratsol Yellow 3GF liq. Product data sheet. 2011. Archroma, Switzerland.
19. Lee, Y. C., Choi, M., Yang, J. W., Shin, H. J., Removal of malachite green (MG) from aqueous solutions by adsorption, precipitation, and alkaline fading using talc: Kinetic, thermodynamic, and column feasibility studies, *Desalin. Water Treat.* **56**(7) (2015) 1918.  
doi: <https://doi.org/10.1080/19443994.2014.951970>
20. Mistron®75-6 KA. Product data sheet. 2011. Imerys S.A. France.
21. Fiume, M. M., Boyer, I., Bergfeld, W. F., Belsito, D. V., Hill, R. A., Klaassen, C. D., Liebler, D. C., Marks, Jr, G. J., Shank, R. C., Slaga, T. J., Snyder, P. W., Andersen, F. A., Safety assessment of talc as used in cosmetics, *Int. J. Toxicol.* **34** (2015) 66S.  
doi: <https://doi.org/10.1177/1091581815586797>
22. Urmínská, B., Derco, J., Zakhar, R., Korpísová, A., Use of zeolites for macronutrients removal from wastewater, *Acta Chim. Slovaca* **12**(1) (2019) 150.  
doi: <https://doi.org/10.2478/acs-2019-0021>
23. Lin, J., Wang, L., Comparison between linear and non-linear forms of pseudo-first-order and pseudo-second-order adsorption kinetic models for the removal of methylene blue by activated carbon, *Front. Environ. Sci. Eng.* **3** (2009) 320.  
doi: <https://doi.org/10.1007/s11783-009-0030-7>
24. Cazetta, A. L., Vargas, A. M., Nogami, E. M., Kunita, M. H., Guilherme, M. R., Martins, A. C., Silva, T. L., Almeida, V. C., NaOH-activated carbon of high surface area produced from coconut shell: Kinetics and equilibrium studies from the methylene blue adsorption, *Chem. Eng. J.* **174**(1) (2011) 117.  
doi: <https://doi.org/10.1016/j.cej.2011.08.058>
25. Hameed, B. H., Din, A. M., Ahmad, A. L., Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies, *J. Hazard. Mater.* **141**(3) (2007) 819.  
doi: <https://doi.org/10.1016/j.jhazmat.2006.07.049>
26. Desta, M. B., Batch sorption experiments: Langmuir and Freundlich isotherm studies for the adsorption of textile metal ions onto teff straw (*Eragrostis tef*) agricultural waste, *J. Thermodyn.* **6**(1) (2013) 1687.  
doi: <https://doi.org/10.1155/2013/375830>
27. Langmuir, I., The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* **40**(9) (1918) 1361.  
doi: <https://doi.org/10.1021/ja02242a004>
28. Alafnan, S., Awotunde, A., Glatz, G., Adjei, S., Alrumaih, I., Gowida, A., Langmuir adsorption isotherm in unconventional resources: Applicability and limitations, *J. Pet. Sci. Eng.* **207** (2021) 109172.  
doi: <https://doi.org/10.1016/j.petrol.2021.109172>
29. Gunawardene, O. H. P., Gunathilake, C. A., Amaraweera, A. P. S. M., Fernando, N. M. L., Manipura, A., Manamperi, W. A., Kulatunga, K. M. A. K., Rajapaksha, S. M., Gamage, A., Dassanayake, R. S., Weerasekara, B. G. N. D., Fernando, P. N. K., Fernando, C. A. N., Jayasinghe, J. A. S. C., Removal of Pb(II) ions from aqueous solution using modified starch, *J. Compos. Sci.* **5**(2) (2021) 46.  
doi: <https://doi.org/10.3390/jcs5020046>
30. Foo, K. Y., Hameed, B. H., Insights into the modeling of adsorption isotherm systems, *Chem. Eng. J.* **156**(1) (2010) 2.  
doi: <https://doi.org/10.1016/j.cej.2009.09.013>
31. Freundlich, H., Heller, W., The adsorption of cis-and trans-azobenzene, *J. Am. Chem. Soc.* **61**(8) (1939) 2228.  
doi: <https://doi.org/10.1021/ja01877a071>

32. *Vigdorowitsch, M., Pchelintsev, A., Tsygankova, L., Tanygina, E.*, Freundlich isotherm: An adsorption model complete framework, *Appl. Sci.* **11**(17) (2021) 8078. doi: <https://doi.org/10.3390/app11178078>
33. *Celebi, O., Üzüm, Ç., Shahwan, T., Erten, H. N.*, A radio-tracer study of the adsorption behavior of aqueous Ba<sup>2+</sup> ions on nanoparticles of zero-valent iron, *J. Hazard. Mater.* **148** (3) (2007) 761. doi: <https://doi.org/10.1016/j.jhazmat.2007.06.122>
34. *Mahanty, B., Behera, S. K., Sahoo, N. K.*, Misinterpretation of Dubinin–Radushkevich isotherm and its implications on adsorption parameter estimates, *Sep. Sci. Technol.* **58**(7) (2023) 1275. doi: <https://doi.org/10.1080/01496395.2023.2189050>
35. *Dubinin, M. M.*, Physical adsorption of gases and vapors in micropores, *Prog. Surf. Sci.* **9** (1975) 1. doi: <https://doi.org/10.1016/B978-0-12-571809-7.50006-1>
36. *Stoeckli, F.*, Dubinin's theory and its contribution to adsorption science, *Russian chemical bulletin* **50**(12) (2001) 2265. doi: <https://doi.org/10.1023/a:1015054922994>
37. *Puccia, V., Avena, M. J.*, On the use of the Dubinin–Radushkevich equation to distinguish between physical and chemical adsorption at the solid-water interface, *Colloid Interface Sci. Commun.* **41** (2021) 100376. doi: <https://doi.org/10.1016/j.colcom.2021.100376>
38. *Darweesh, M. A., Elgendy, M. Y., Ayad, M. I., Ahmed, A. M. M., Elsayed, N. K., Hammad, W. A.*, A unique, inexpensive, and abundantly available adsorbent: Composite of synthesized silver nanoparticles (AgNPs) and banana leaves powder (BLP), *Heliyon* **8**(4) (2022) e09279. doi: <https://doi.org/10.1016/j.heliyon.2022.e09279>
39. *Didier de Vasconcelos, G. M., Mulinari, J., de Arruda Guelli Ulson de Souza, S. M., Ulson de Souza, A. A., de Oliveira, D., de Andrade, C. J.*, Biodegradation of azo dye-containing wastewater by activated sludge: A critical review, *World J. Microbiol. Biotechnol.* **37**(6) (2021) 101. doi: <https://doi.org/10.1007/s11274-021-03067-6>
40. *Zou, C. L., Liang, J. Y., Jiang, W., Guan, Y. Y., Zhang, Y. C.*, Adsorption behavior of magnetic bentonite for removing Hg(II) from aqueous solutions, *RSC Adv.* **8** (2018) 27587. doi: <https://doi.org/10.1039/c8ra05247f>
41. *Oussalah, A., Boukerroui, A., Aichour, A., Djellouli, B.*, Cationic and anionic dyes removal by low-cost hybrid alginate/natural bentonite composite beads: Adsorption and reusability studies, *Int. J. Biol. Macromol.* **124** (2019) 854. doi: <https://doi.org/10.1016/j.ijbiomac.2018.11.197>