

Original Research

REMOVAL OF SYNTHETIC DYE FROM AQUEOUS SOLUTIONS USING
Quercus cerris ACORN CUPS

DOI: 10.5937/EcoTER26250N

Milena Nikolić^{1,a*}, Aleksandar Zdravković^{1,b}, Dragana Marković Nikolić^{1,c},
Goran Petković^{1,d}, Tanja Nikolić^{1,e}

¹Academy of Applied Studies of Southern Serbia, Department of Higher Technology and Art School,
Vilema Pušmana 17, 16000 Leskovac, SERBIA

^a <https://orcid.org/0000-0002-6631-936X>

^b <https://orcid.org/0000-0001-9906-3543>

^c <https://orcid.org/0000-0003-3171-9838>

^d <https://orcid.org/0009-0001-4375-2857>

^e <https://orcid.org/0009-0007-8932-6128>

Abstract

The aim of this research was to examine the potential application of the biosorbent obtained from the oak acorn cups (lat. *Quercus cerris*) to remove the methylene blue from aqueous model solutions. The following parameters were optimized: pH values, biosorbent dose and initial concentrations of methylene blue. The highest sorption capacity of this sorbent towards methylene blue was achieved at following conditions: pH 8, initial concentration of methylene blue 25 mg/dm³, biosorbent dose 9 g/dm³. After linear fitting, the experimental kinetic data fitted pseudo-second order model.

Keywords: biosorbent, *Quercus cerris*, methylene blue, pseudo-second order kinetics.

INTRODUCTION

Quercus cerris occupies drier and moderately fertile habitats in lowland and hilly areas of Serbia, where large forests with other species of oak and hornbeam are formed.

Due to lower technological quality, different color of its core part and its tendency to crack, *Quercus cerris* wood is not adequate for industrial processing. It is used as firewood, because of the similar calorific value as hornbeam and beech. However, the main advantage is that it can be used in soil conservation, erosion suppression and reforestation of bare lands due to its strong and branched root system [1]. *Quercus cerris* is often planted in urban areas as an ornamental tree because of its attractive and well-shaped canopy. Furthermore, acorns represent a potential resource in the food industry. Gluten-free and nutritive-valuable flour obtained from acorns was found to be rich in essential unsaturated fatty acids (oleic and linoleic acid), minerals (K, Mg, P, Ca, Fe, Mn) and phenolic compounds with conspicuous antioxidative effect (gallic and syringic acids, catechin, flavanols) [2]. Due to its physicochemical characteristics, flour can be used for preparation of bread [3] and biscuits [4]. However, acorn caps cannot be used in human diet, therefore are discarded but suitable for investigation and discovering new ways of use.

* milenai.chem@gmail.com

Methylene blue is a cationic dye used for food and pharmaceutical industries but even more for wool, silk, temporary hair dyes, cotton and textile [5]. Wastewater produced from the textile industry often contains a mixture of several colors and may cause serious health and environmental problems [6]. Thermal and photostability of dye in the environment affects the absorption and reflection of sunlight, which reduces the intensity of photosynthesis in aquatic bodies and causes disturbances in the natural food chain. Therefore, the inevitable impact of these pollutants requires treatment before discharge into the mainstream and causes environmental degradation. Outpouring of colored wastewater into the ecosystem causes eutrophication, aesthetic pollution and disturbance of aquatic life [7]. Although antioxidant, cardio-protective, antimalarial and antidepressant properties have been demonstrated in therapeutic doses, long-term exposure to methylene blue can also cause health problems such as anemia, cancer, vomiting, eye irritation, nausea [8].

Based on the above facts, the aim of this research was to investigate the potential application of a biosorbent derived from *Quercus cerris* acorn caps (QC) for the removal of methylene blue from the aquatic environment. According to our knowledge, there are no available studies published regarding biosorption of pollutants onto this type of sorbent.

MATERIALS AND METHODS

Biosorbent preparation and characterization

Fully ripe acorns of the *Quercus cerris* were collected in the vicinity of Leskovac, in the Pusta Reka region. The caps were separated from the acorns for more efficient drying and left in a well-ventilated place for a month, then coarsely crushed in a porcelain mortar, ground in a laboratory blender and sieved on a laboratory sieve with 1 mm diameter. The QC biosorbent was then used in sorption experiments. Evaluation of QC biosorbent was performed according to iodine number method [9]. Point of zero charge (pH_{pzc}) was determined by mixing 0.05 g of QC biosorbent and 20 mL of 0.1 M KCl and varying the pH from 2 to 12 using HCl or NaOH. The pH values were measured by digital pH meter (HI-2209, Hanna, USA).

Sorption experiments

The sorption study was conducted in order to analyze the effect of pH, biosorbent dose and initial concentration of methylene blue. Deionized water was used for preparation of all solutions. The concentration of methylene blue was measured spectrophotometrically at 620 nm. The removal efficiency (%) was calculated according to the Equation 1:

$$\% = (c_0 - c_t) / c_0 * 100 \quad (1)$$

RESULTS AND DISCUSSION

The material and reagents for measuring iodine number are not expensive, and the time required to perform the analysis is relatively short. The QC biosorbent was evaluated using the iodine number method, with the result yielding $q_i = 195.4 \text{ mg/g}$. Since used in native condition, lower value of iodine number may indicate a low microporosity of the surface of the biosorbent, but this could undoubtedly be improved by chemical or thermal modification.

One of the most important factors affecting the efficiency of the sorption process is the pH value of the aquatic environment, due to the influence (protonation/deprotonation) on the

functional groups of the pollutants as well as the sorbent [10]. The pH_{pzc} for QC biosorbent was found to be 6.23 meaning its surface will be negatively charged at higher pH values. Since methylene blue is a cationic dye, it is expected for alkaline conditions to be favorable for its sorption onto QC biosorbent. The influence of pH on the removal of methylene blue from the water was examined in the range of pH values from 2 to 12 with other parameters as follows: initial concentration of methylene blue 25 mg/dm^3 , QC biosorbent dose 5 g/dm^3 . The greatest removal efficiency occurred at pH 8, and increased negligibly with further increase of pH, (Figure 1) therefore this value was chosen for further investigations. Higher sorption capacity of methylene blue in alkaline conditions was also reported for sorbents obtained from *Osmanthus fragrans* [11] and *Stipa tenacissima* plants [12].

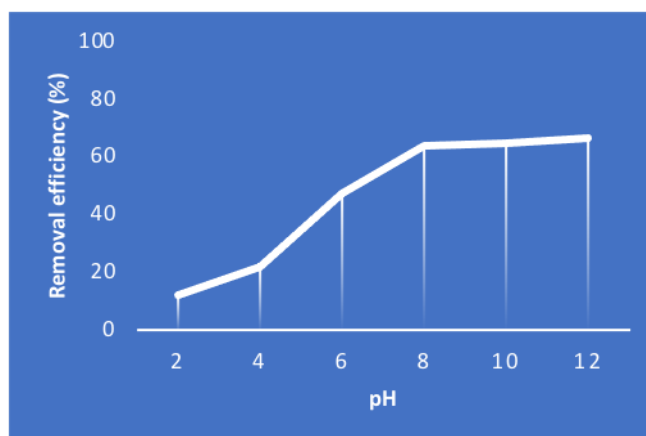


Figure 1 The methylene blue removal efficiency as a function of pH

The effect of biosorbent dose on removal efficiency of methylene blue was investigated at pH 8 and initial concentration of methylene blue 25 mg/dm^3 and is represented in Figure 2. As it can be seen, increase in biosorbent dose (up to 9 g/dm^3) led to greater removal efficiency (up to 83.6%) due to greater number of binding sites on the surface of the QC biosorbent.

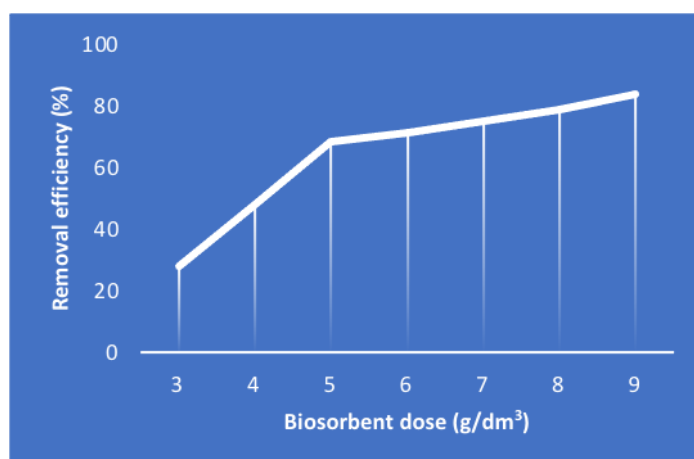


Figure 2 Effect of biosorbent dose on removal efficiency of methylene blue

The initial concentration is an important kinetic parameter for the process of binding the polluting substance to the binding spots of the biosorbent. The influence of the initial

concentration of methylene blue on its removal from an aqueous solution by QC biosorbent was investigated at initial concentrations of methylene blue from 5 to 65 mg/dm³ at pH 8, and QC biosorbent dose 9.0 g/dm³. The result is shown in Figure 3. At lower concentrations of methylene blue, sufficient number of binding spots on the surface of the QC biosorbent were available and the removal efficiency was 87.4%, 69.3% and 63.6% for 5, 15 and 25 mg/dm³. As the concentration increased the binding sites were saturated, and the removal efficiency dropped significantly with a further increase in the initial concentration of methylene blue, yielding only 17% for 65 mg/dm³.

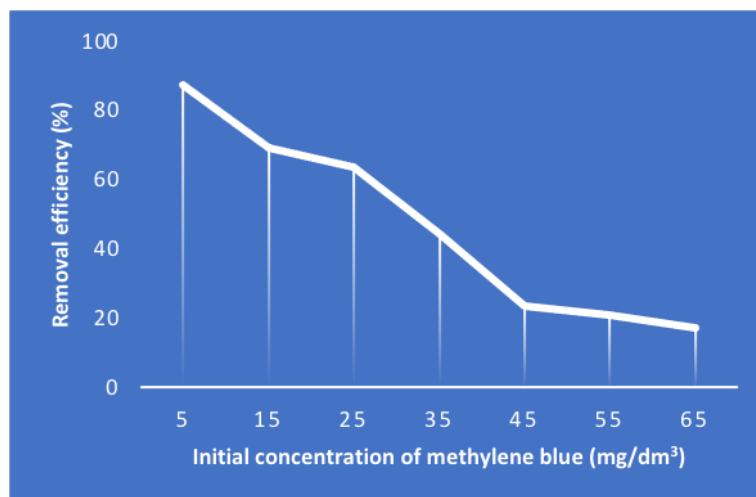


Figure 3 Effect of initial concentration on removal efficiency of methylene blue

The sorption capacity of QC biosorbent towards methylene blue over time, q_t (mg/g), was calculated according to the Equation 2:

$$q_t = \frac{(c_0 - c_t)V}{m} \quad (2)$$

where c_0 and c_t represent the initial concentration and concentration of the methylene blue solution in time t (mg/dm³), respectively, V volume of the methylene blue solution (dm³), and m the mass of the QC biosorbent (g).

A model suitable for describing the kinetics of the sorption process can be determined based on experimentally obtained sorption capacities. Pseudo-first order (Equation 3) and pseudo-second order (Equation 4) kinetic models are the most often used to determine the order of the reaction and the rate constant of the sorption process.

$$dq_t/dt = k_1(q_e - q_t) \quad (3)$$

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (4)$$

where k_1 (1/min) is the pseudo-first-order rate constant, k_2 (g/mg min) is the pseudo-second-order rate constant, q_t (mg/g) is the sorbent capacity at time t , and q_e (mg/g) is the sorbent capacity in the equilibrium state.

According to Equation 3, the results were obtained for the pseudo-first order kinetics and presented in the Figure 4.

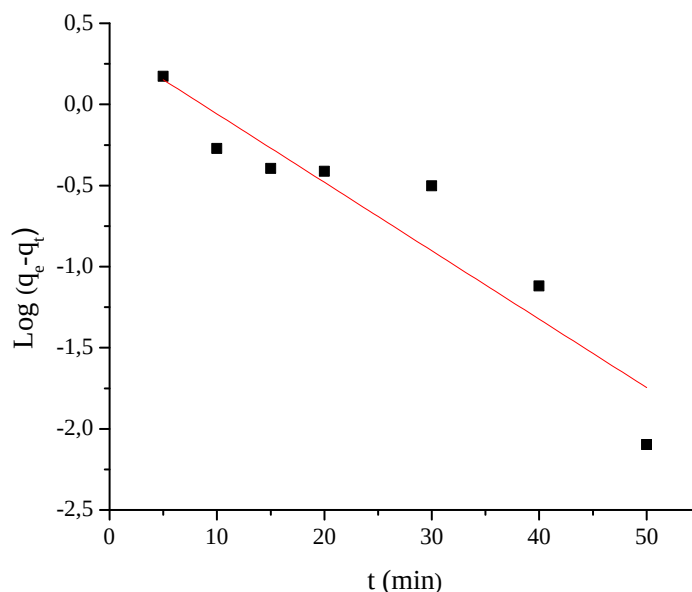


Figure 4 Kinetic model of pseudo-first order

According to Equation 4, the results were obtained for the pseudo-second order kinetics and presented in the Figure 5.

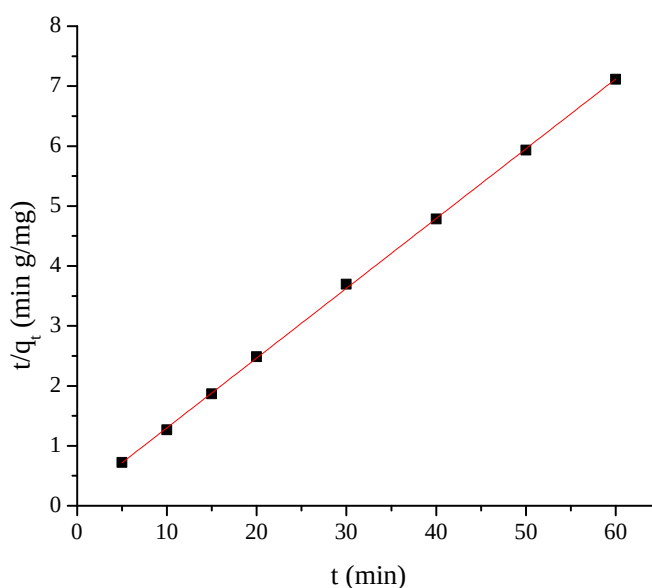


Figure 5 Kinetic model of pseudo-second order

The software package Origin Pro 8.0 (OriginLab Corporation, USA) was applied for linear fitting of experimental data and the kinetic parameter values are given in Table 1.

According to the linear curves in the Figures 4 and 5 and the correlation coefficients in Table 1, it is evident that the sorption of methylene blue onto QC biosorbent follows pseudo-second order kinetics. The correlation coefficient for the pseudo-second order model is higher than the correlation coefficient for the pseudo-first order model. The value of the

calculated sorption capacity according to the pseudo-second-order model ($q_{e,cal}=8.594$ mg/g) is significantly closer to the experimental sorption capacity ($q_{e,eks}=8.436$ mg/g), than the value of the calculated sorption capacity according to the pseudo-first order model ($q_{e,cal}=2.308$ mg/g).

Table 1 Kinetic parameters of sorption models of methylene blue

Kinetic model	Parameter	Methylene blue
Eksperimental	$q_{e,exp}$ (mg/g)	8.436
	$q_{e,cal}$ (mg/g)	2.308
Pseudo-first order	k_1 (1/min)	9.71
	R^2	0.8567
Pseudo-second order	$q_{e,cal}$ (mg/g)	8.594
	$k_2 \times 10^3$ (g/mg min)	9.87
	R^2	0.9997

CONCLUSION

Quercus cerris acorn caps were used for biosorption of cationic dye methylene blue from aqueous media. Biosorbent was used in native condition. Sorption of methylene blue onto QC biosorbent followed pseudo-second order kinetics.

The point zero charge of biosorbent was at pH 6.23, thus alkaline conditions were favorable for sorption of methylene blue. Also, biosorption was notably influenced by biosorbent dose and initial concentration of methylene blue. Even though potential usage of QC biosorbent in native condition was estimated, the study highlighted its potential to be chemically or thermally modified in order to improve its sorption properties.

REFERENCES

- [1] de Rigo D, Enescu CM, Houston Durrant T *et al.* *Quercus cerris* in Europe: distribution, habitat, usage and threats. In: San-Miguel-Ayanz J, de Rigo D, Caudullo, G, Houston Durrant, T, Mauri, A, editors. *European Atlas of Forest Tree Species*. Luxembourg, European Commission; 2016. p. 148.
- [2] Martins, R.B., Gouvinhas, I., Nunes, M.C., *et al.* *Curr. Res. Food Sci.* 2022, 5, 2211–2218.
- [3] Skendi, A., Mouselemidou, P., Papageorgiou, M., *et al.* *Food Chem.* 2018, 253, 119–126.
- [4] Korus, A., Gumul, D., Krystyjan, M., *et al.* *Eur. Food Res. Technol.* 2017, 243 (8), 1429–1438.
- [5] Khan, I., Saeed, K., Zekker, I., *et al.* *Water.* 2022, 14(2), 242.
- [6] Wang, X., Jiang, J., Gao, W. *Water Sci Technol.* 2022, 85 (7), 2076–2096.
- [7] Holkar, C.R., Jadhav, A.J., Pinjari, D.V., *et al.* *J. Environ. Manage.* 2016, 182, 351–366.
- [8] Fito, J., Abewaa, M., Mengistu, A. *Sci. Rep.* 2023, 13, 5427.
- [9] Du, C., Liu, B., Hu, J. *et al.* *Mater. Lett.* 2021, 285, 129–137.
- [10] Banerjee, S., Chattopadhyaya, M.C. *Arab J of Chem.* 2017, 10, S1629–S1638
- [11] Chai, B., Cheng, X., Ren Z., *et al.* *Desalin. Water Treat.* 2016, 57, 18868–18878.
- [12] Ladjali, S., Dahdouh, N., Amokrane, S., *et al.* *APTEFF.* 2021, 52, 33–44.