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Adsorption behavior of methylene blue onto four different coffee residues

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Abstract

In this study, the adsorption of methylene blue dyestuff in aqueous solution was investigated by using four different types of waste coffee grounds. The four coffee residues were Jacobs Monarch Coffee, Tchibo Professional Special Filter Coffee, Turkish Coffee (Mehmet Efendi), and Anisah Guatemala Coffee. Adsorption mechanisms were investigated by applying different adsorption conditions such as contact time, pH, methylene blue concentration and temperature. The characterization of the samples (before and after adsorption with methylene blue) was performed using FTIR and SEM analyses. The FTIR findings showed that methylene blue bonded with the hydrogen bonds. Langmuir and Freundlich isotherms were preferred to determine the adsorption mechanisms. When the results obtained are examined, it is seen that the maximum adsorption capacity was 67.14 mg/g at 298 K for Turkish coffee. It is understood that waste coffee grounds (especially Turkish coffee) are a cost-effective and environmentally friendly material for the removal of methylene blue in aqueous solution.

Keywords: Adsorption, Coffee Residue, Methylene Blue.

1. Introduction

As a result of increasing industrialization, environmental pollution has been increasing, also creating many problems by affecting living organisms [1]. Dyes are colored with organic compounds that give color to surfaces and fabrics [2]. These wastes can be classified as dyestuffs, heavy metals, organic and inorganic pollutants. Synthetic dyes are preferred in many different industrial areas such as textile, food processing, paper, plastic and cosmetics. [3]. With the discharge of dyes, both terrestrial and aquatic life are endangered. This causes a serious problem [4]. Physical, chemical and biological methods can be used to treat dyes [5]. Among these methods, the adsorption method is the most effective methods for removing many synthetic and organic substances in water. Because it is very high efficiency and adaptability [6]. Adsorption or adhesion is a chemical and physical force related to the surface. Adsorption is a very efficient process for remove pollutants [7]. In adsorption methods, especially activated carbon, some polymer-derived adsorbents and other low-cost (waste) materials are widely preferred [8]. There are many studies that used a variety of materials such as banana peel and orange peel [9], *Terminalia catappa* Shell [10], corn cub [11], *Ulva lactuca* [12] and *Cystoseira barbata* [13].

The most existing dye's chemical structure is quite complex, but remains stable when exposed to light, heat, and oxidizing agents. To eliminate this complexity, paints maintain their stable form when exposed to factors such as light, heat, and oxidizing agents. One of the water-soluble dyes is methylene blue (MB). Methylene blue is used in many different areas such as cotton, wood, leather and drug dyeing. [14]. Although methylene blue does not cause a very high level of toxic effects in the aquatic system, it still causes negative effects such as rapid or difficult breathing, nausea, vomiting, diarrhea, and gastritis [15].

The aim of this study is to investigate the maximum adsorption capacities of four different waste coffee grounds used as adsorbent for the adsorption of methylene blue in aqueous solution. The study of various factors affecting the adsorption, such as pH, contact time, different concentrations of methylene blue, and three different temperatures, were carried out. Different adsorption conditions have been optimized to achieve maximum adsorption capacity. Freundlich and Langmuir isotherm models were used to explain the adsorption mechanism. Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscopes (SEM) analysis were preferred to understand the bonding structure and surface of the coffee grounds.

Although there are different studies with coffee [16-20] et al., 2021), there is no study on Turkish coffee. Therefore, this study is the first to include Turkish coffee on the comparison of different coffees.

2. Materials and Methods

2.1. Preparation of the Adsorbent

The coffee residues were provided by Jacobs Monarch Coffee Company, Tchibo Professional Special Filter Coffee, Turkish Coffee (Mehmet Efendi), and Anisah Guatemala Coffee, which were used as a filter. Waste coffee grounds were cleaned with distilled water and dried at 60°C for 24 hours.

2.2. Reagent and Equipment

Information about coffee and MB was given in Table 1. For the adsorption experiments, 1000 ppm stock MB solution was prepared and MB solutions (5, 10, 20, 50, 100, 150 and 200 mg/L) were obtained at different concentrations from the stock MB solution. pH adjustments with 0.1 M HCl and 0.1 M NaOH aqueous solutions. The samples were shaken with Mikrotest MSC 30 model shaker. MB concentration in solution was determined at 665 nm with a Specord S 600, Analytical Jena spectrophotometer.

2.3. Batch Biosorption Studies

10 mg of different coffee waste grounds were added to 10 mL of methylene blue (MB) solutions (10 ppm) of different pH standards. It was shaken at 250 rpm at 298 K for 60 minutes and then measured by spectrophotometer. All adsorption experiments were performed in three repetitions. % Removal (R) of MB removed from the aqueous solution was calculated by applying the following equation:

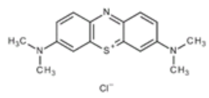
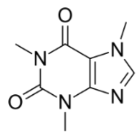
$$\% \text{ Removal (R)} = \frac{(C_o - C_e)}{C_o} * 100 \qquad \textbf{(2.1)}$$

where C_o is the initial MB concentration (mg/L) and C_e is the equilibrium MB concentration in the aqueous solution (mg/L).

2.4. Determining the pH Effect

Studies were performed at different pHs (2, 3, 5, 7 and 9) at a fixed initial concentration (10 ppm). The samples were shaken at 250 rpm at 298 K for 60 minutes and the R-value was again calculated using Equation. (2.1).

Table 1. Information on methylene blue and coffee**.**

Descriptive factor	**Methylene blue**	**Coffee**
Chemical formulation	$C_{16}H_{18}N_3SCl$	$C_8H_{10}N_4O_2$
Molecular weight	319.85 $gmol^{-1}$	194.94 $gmol^{-1}$
Chemical structure		

2.5. Determining the time effect

Biosorption studies were performed at room temperature at different contact time from 10 minutes to 300 minutes (10, 25, 50, 100, 150, 200 and 300 minutes). The MB uptake at each time interval, qt (mg/g), was calculated by applying the equation given below:

$$qt = \frac{(C_o - C_e)}{M} * V \qquad \textbf{(2.2)}$$

where C_o is the initial MB concentration (mg/L), C_e is the concentration of MB at a given time (mg/L), V is the volume of the MB solution (L), and M is the mass of the coffee (g dry weight).

2.6. Determining the Ion Concentration Effects

In the adsorption process, 100 mg of different percentages of coffee was added and with 10 mL of MB solution at an optimum pH for each coffee at different concentrations (5, 10, 20, 50, 100, 150, and 200 mg/L) at 25, 35, or 45 °C. The quantity of MB was derived from the concentration change at each temperature.

2.7. Characterizing Biomass

FTIR and SEM analysis were preferred for the analysis of the surface structures of the coffee groups. For FTIR and SEM analysis, each of the coffee batches was dried at 60 °C for 24 hours. A scanning electron microscope (Jeol JSM 7100F) was used to understand the changes in the adsorption process.

3. Results and Discussion

3.1. Determining the pH Effect

The pH of a dye solution is important because the performance of adsorption is dependent on the pH. pH affected the surface charge and protonation and deprotonation reaction were occurred [21]. The pH-dependent adsorption of MB with waste coffee grounds in aqueous solution is shown in Figure 1.

With the increasing pH, the proportion of negative charge in coffee molecules increased. As can be seen in Figure 1, with the change of pH, the adsorption capacity changed. The maximum adsorption capacity was 90% for Jacobs (at pH 3), 87% for Tchibo (at pH 5), 90% for Turkish coffee (at pH 9) and 83% for Anisah (at pH 9). A similar behavior has been given by other MB adsorption studies [22-24].

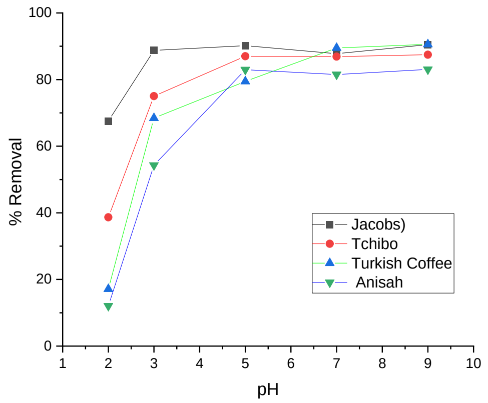


Figure 1. Effect of pH on the biosorption of methylene blue (MB).

3.2. Determining the Time Effects

The contact time has a great influence on the adsorption studies. As seen in Figure 2, adsorption takes place in 100 minutes for Turkish coffee, 150 minutes for Tchibo, and 200 minutes for Anisah and Jacobs coffees.
This is stated that methylene blue adsorption occurs mainly on the surface of the waste coffee grounds as given by other studies on adsorption of methylene blue [23].

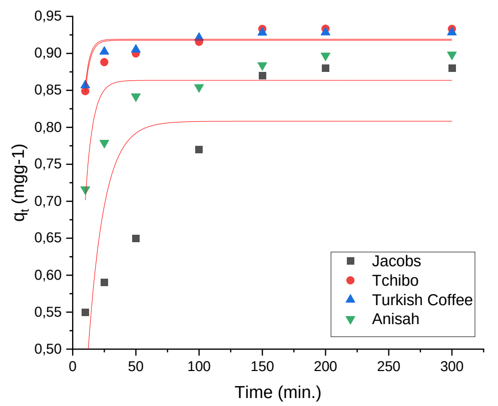


Figure 2. Effects of time on the biosorption of MB (pH 3) by different concentrations of four coffee residues.

3.3. Adsorption isotherms

Langmuir and Freundlich isotherm models were used for equilibrium description. The Langmuir model [25] is shown below:

$$\frac{C_e}{q_e} = \frac{1}{q_m a_L} + \frac{C_e}{q_m} \qquad \textbf{(3.1)}$$

where qe (mg/g) and Ce (mg/L) correspond to the concentration of MB adsorbed per gram of biomass and present in aqueous solution. q_m (mg/g) is the maximum adsorption capacity, and a_L is the Langmuir constant related to the adsorption energy.

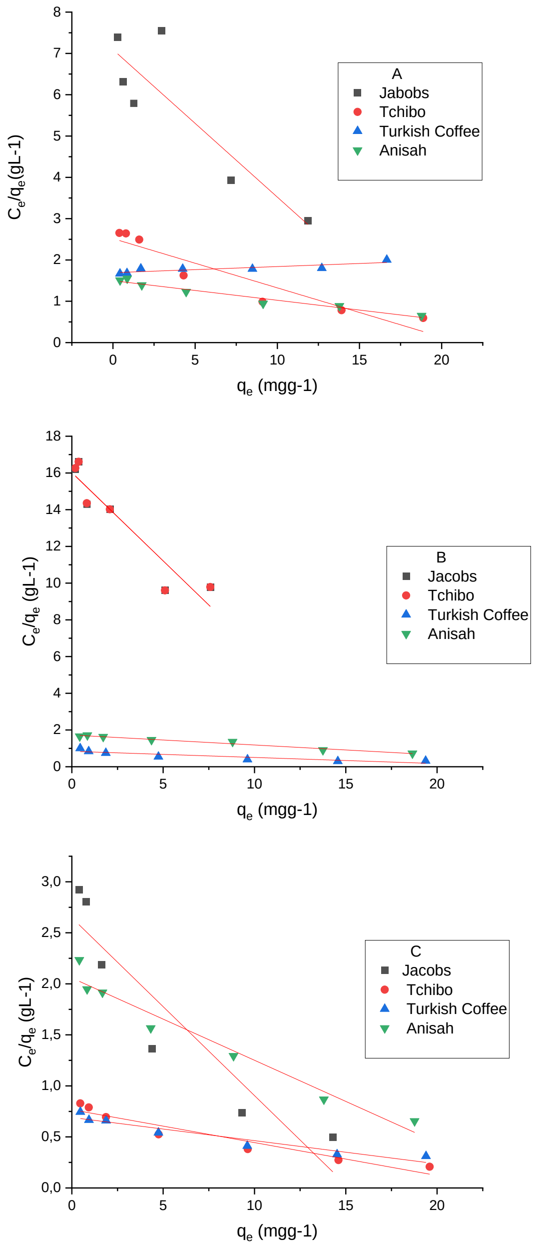


Figure 3. Adsorption isotherm curves for MB at 298 K (A), 308 K (B), and 318 K (C) at different concentrations of four coffee residues.

A linear form of Freundlich's equation is shown below [26] is shown below:

$$\log q_e = \log K_f + 1/n_f \log C_e \qquad \textbf{(3.2)}$$

Given in this equation, K_f represents the adsorption capacity and n_f is related to adsorption. Linear regression using Langmuir and Freundlich isotherm models, equilibrium data at different concentrations and at three different temperatures were customized as seen in Figure 3 and Table 2.

As can be seen from Table 2, for all coffee species, for every temperature, the Freundlich adsorption isotherm gave a better fit than the Langmuir model based on the correlation coefficient (R^2) value (up to 0.93). Looking at these results, it can be understood that MB adsorption belongs to the physical adsorption group.

The highest q_{max} value for Jacobs and Tchibo coffees was at 318 K, and was 5.74 mg/g and 30.96 mg/g, respectively. However, when the temperature increased, the q_{max} value of Turkish coffee first decreased and then increased (67.14 mg/g to 29.85 mg/g and to 44.05 mg/g). For Anisah, the q_{max} value increased with temperature (21.09 mg/g – 18.45 mg/g – 12.41 mg/g). From these results, we can say that the temperature affected the maximum adsorption capacity for each coffee species. The highest adsorption capacity was 67.14 mg/g (at 298 K).

Table 2. Parameters of Langmuir and Freundlich isotherms of MB adsorption at different concentrations of four different waste coffee grounds.

		Langmuir isotherm models			**Freundlich isotherm models**		
Adsorbent	**Temperature(K)**	q_{max} **(mg/g)**	a_L	R_L^2	n_f	K_f **(mg/)**	R_F^2
Jacobs	298	1.83	0.082	0.7012	0.89	0.128	0.9684
	308	1.04	0.059	0.8867	0.85	0.046	0.9949
	318	5.74	0.066	0.8710	0.54	0.225	0.9312
Tchibo	298	8.34	0.047	0.8870	0.63	0.267	0.9574
	308	1.04	0.060	0.8888	0.85	0.046	0.9949
	318	30.96	0.042	0.9248	0.66	1.584	0.9693
Turkish Coffee	298	67.14	0.009	0.7375	1.04	0.596	0.9995
	308	29.85	0.039	0.8098	0.67	1.325	0.992
	318	44.05	0.033	0.9207	0.77	1.665	0.9917
Anisah	298	21.09	0.032	0.9560	0.79	0.634	0.9889
	308	18.45	0.032	0.9761	0.82	0.556	0.9775
	318	12.41	0.039	0.958	0.73	2.44	0.9722

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Table 3. Comparison of adsorption capacities of MB in various adsorbents

Adsorbent	q_m **(m/g)**	**Reference**
Coffee grounds	18.73	[23]
Banana peel	21.0	[9]
Orange peel	20.5	[9]
Wheat shells	16.6	[27]
Coffee husk	20.95	[28]
Ipomoea carnea	83.87	[29]
Corn stigmata	106.3	[30]
Sargassum latifolium	8.54	[31]
Jacobs Coffee	5.74	**This study**
Tchibo Coffee	30.96	**This study**
Turkish Coffee	67.14	**This study**
Anisah Coffee	21.09	**This study**

3.4. Characterizing Biomass

3.4.1. FTIR Study

The functional groups of different coffee residues were shown in Table 4 and Figure 4. The peak around 3300 cm^{-1} is the stretching band of OH in water [32]. The sharp peak at 1744 cm^{-1} is attributed to the stretching of the carbonyl groups [1]. The OH peak is seen at around 2360 cm^{-1}. The CH-OH bending peak is seen at 1455 cm^{-1} [33].

It can be seen that when coffee species adsorbed MB, the peaks shifts were observed in these peaks. As a result, the hydrogen bonds were responsible for the adsorption of MB.

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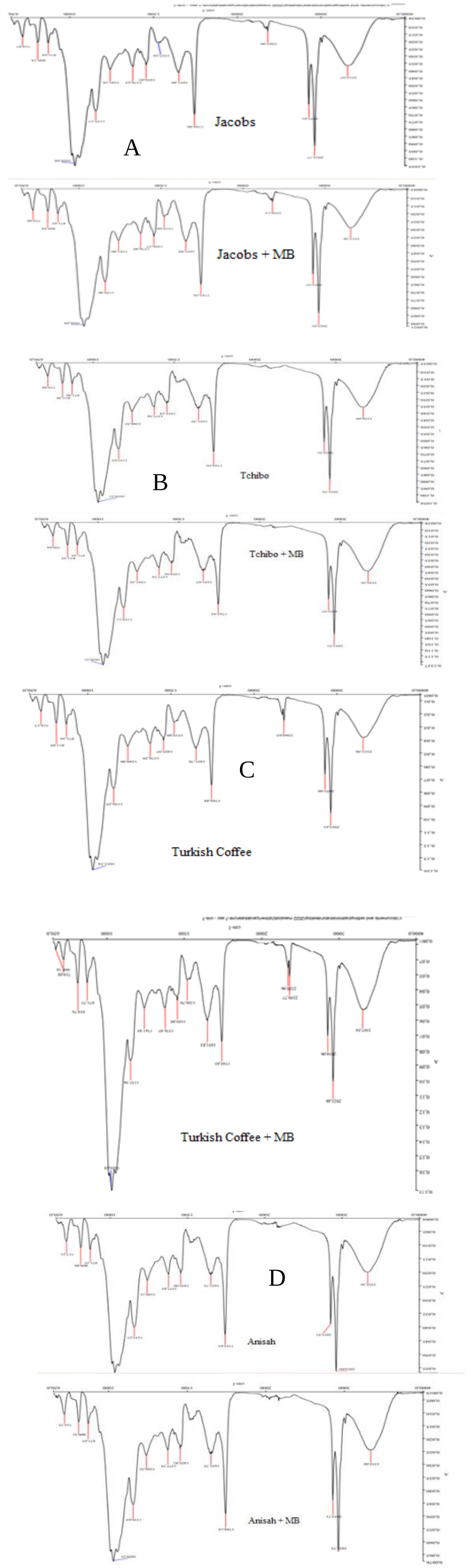

Figure 4. FTIR spectra of (A) Jacobs, (B) Tchibo, (C) Turkish Coffee and (D) Anisah.

Table 4. Functional groups in the FTIR analyses of the waste coffee grounds.

Functional group	Wavenumber (cm^{-1})			
	Jacobs	Tchibo	Turkish Coffee	Anisah
–OH groups in water molecule	3315	3366	3313	3332
-CH stretching	2923	2923	2923	2923
-OH	2363	2358	2360	2360
C = O carbonyl groups	1744	1744	1744	1746
Amide C=N and C=C stretches	1651	1651	1651	1651
CH-OH bending	1456	1455	1455	1455
Amide C-N	1376	1377	1367	1377
C-O carboxyl	1241	1240	1240	1240
Symmetric stretching vibration of the C-O-C	1155	1157	1156	1155

3.4.2. SEM study

The SEM and EDX micrographs of the four species of coffee residues before and after the adsorbed MB dye were presented in Fig. 5. In Figure 5, a is Jacobs, b is Jacobs after MB adsorption, c is Turkish coffee, d is Turkish coffee after MB adsorption, e is Anisah, f is Anisah after MB adsorption, g is Tchibo, and h is Tchibo after MB adsorption. For the SEM analysis, it was seen that the surface of each coffee was different. It was understood that the coffee with the most indented surface was Turkish coffee.

Considering the EDX analyses, the elemental analyses of the coffee varieties were also different. Considering the EDX analyses, the elemental analyses of the coffee varieties were also different. It was observed that there was a change in the elemental analysis as a result of MB adsorption. It was thought that the adsorption capacity of Turkish coffee was higher due to its structure and surface being more protruding.

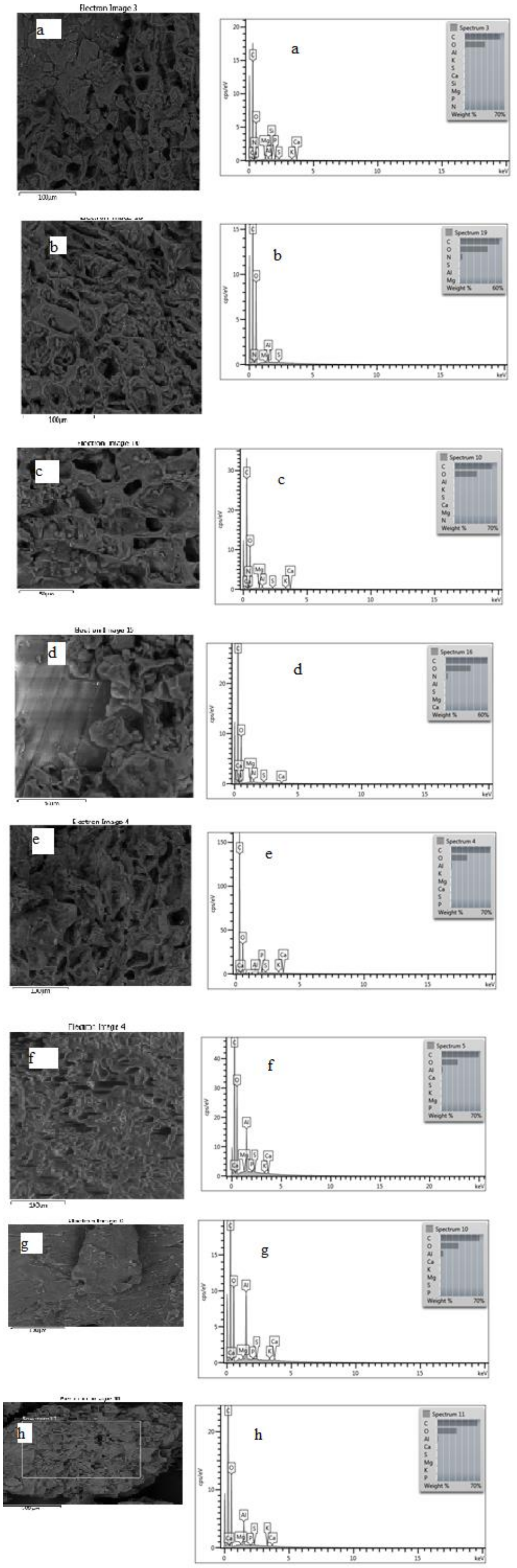

Figure 5. SEM and EDX micrographs of the four species of coffees, before and after adsorbed MB.

4. Conclusion

The residues of four different coffee species were prepared and applied to remove methylene blue (MB) from aqueous solution. The adsorption efficiency, such as, pH, contact time, concentration and temperature, were investigated. For each group of coffee, the removal % of MB was increased with pH and the maximum adsorption capacities were, pH 3 for Jacobs, pH 5 for Tchibo and pH 9 was Turkish and Anisah. Adsorption rate was fast, arrived adsorption balance within about 1000 min. The maximum adsorption capacity was 67.14 mg/g at 298 K for Turkish coffee. The Freundlich model was appropriate to represent the equilibrium data. The coffee surfaces of the adsorbent were confirmed by the FTIR analysis. For the FTIR analysis, the hydrogen bonds were responsible for MB adsorption. Moreover, the SEM revealed that the surface heterogeneity of the coffees was reduced after the adsorption of MB. Briefly, we can say that especially Turkish coffee is a readily available and eco-friendly adsorbent for removing MB.

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Author's Contributions

Ecem Tekne, **Yeliz Özüdoğru:** Drafted and wrote the manuscript, and performed the experiment and result analysis.

Ecem Tekne, **Yeliz Özüdoğru:** Assisted in analytical analysis on the structure, supervised the experiment's progress and result interpretation, and helped the manuscript preparation.

Ethics

There are no ethical issues regarding the publication of this manuscript.

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