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ORIGINAL ARTICLE

# Langmuir and Freundlich Isoterm Adsorption Using *Citrus reticulata* Peel as A Potential Biosorbent for Dye Removal

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**ABSTRACT -** Textile processes generate huge amounts of dyes. Biosorbent from *Citrus reticulata* is effective in removing dyes from wastewaters as it is cost-effective, efficient, and easy. Approximately 50 g of *Citrus reticulata* peel was dried at 50°C for 24 hours and later milled and sieved to a particle size of 250 µm. This study aims to determine the appropriate adsorption isotherm model in the adsorption process to reduce dye concentration of methylene blue with various parameters of pH, sorbent dosage and contact time. All these adsorption studies under diferent parameters were observed using UV-Vis spectrophotometer measured at 665nm. The data collected was used to identify the isotherm model that fit the biosorption mechanism of methylene blue dye. The results in this study showed that the optimum conditions for maximum removal of methylene blue dye are at pH 9, 0.5 g of biosorbent dosage, 100 ppm initial methylene concentration at 15 to 30 minutes of contact time. Langmuir isotherm with higher $R^2$ value of 0.9577 was determined to be the biosorption mechanism of *Citrus reticulata* biosorbent on methylene blue dye removal. Thus, *Citrus reticulate* served as a potential alternative method for dye removal.

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## INTRODUCTION

Water pollution arises from various sources, with industrial discharge being a major contributor. Among these, textile wastewater is particularly concerning due to the large quantities of synthetic dyes it contains. These dyes pose significant risks to both the environment and human health. Environmentally, dyes can inhibit photosynthesis in aquatic plants by obstructing sunlight penetration, and their high turbidity reduces dissolved oxygen availability, threatening the survival of aquatic organisms [1]. From a human health perspective, certain dyes such as azo dyes commonly used in the textile industry have been linked to carcinogenicity, genotoxicity, and reproductive toxicity [1].

Given these risks, it is essential to remove dyes from textile effluents prior to discharge into natural water bodies. Several treatment methods have been developed for this purpose, including adsorption, ion exchange, and membrane filtration [2]. Among these, adsorption is considered effective and widely applicable. Activated carbon is the most commonly used adsorbent for dye removal from aqueous solutions due to its high adsorption capacity. However, its high production and regeneration costs hinder its practical application in large-scale wastewater treatment. Consequently, there is growing interest in identifying cost-effective and sustainable alternatives to activated carbon for dye removal [3].

In recent years, increasing attention has been paid to the use of agricultural waste as biosorbents for wastewater treatment. Materials such as rice husk, banana peel, coconut shell, and orange peel have shown promising adsorption capacities for various dyes [3]. These materials are renewable,

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biodegradable, and abundantly available, making them economically and environmentally attractive options. *Citrus reticulata* (mandarin orange) peel is a type of agro-industrial waste rich in lignocellulosic content, including cellulose, hemicellulose, and pectin, which contain functional groups such as hydroxyl, carboxyl, and methoxyl groups capable of binding dye molecules. Several studies have demonstrated the potential of citrus peels for adsorbing cationic dyes like methylene blue through mechanisms such as electrostatic attraction, ion exchange, and hydrogen bonding [4]. Pre-treatment methods, including drying, grinding, or chemical activation, have been reported to enhance the adsorption efficiency by increasing surface area and improving porosity [5].

Methylene blue (MB) is a cationic dye widely used in textile, paper, and leather industries. It is often employed as a model compound in adsorption studies due to its well-defined structure, stability in aqueous solution, and ease of detection through spectrophotometry [6]. The removal of MB from water has been extensively studied using various biosorbents, making it a reliable benchmark for evaluating adsorption performance. To understand the interaction between adsorbate and adsorbent, several isotherm models have been applied in dye adsorption studies. The Langmuir isotherm assumes monolayer adsorption onto a surface with a finite number of identical sites, suggesting a uniform adsorption process [7]. It is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \left(\frac{1}{q_{max}}\right) C_e$$

Where, qe is the amount adsorbed at equilibrium (mg/g), qmax is the maximum adsorption capacity (mg/g), Ce is the equilibrium concentration of dye (mg/L), and b is the Langmuir constant related to binding affinity. In contrast, the Freundlich isotherm describes multilayer adsorption on heterogeneous surfaces, suitable for systems with varying binding affinities [7]. It is expressed as:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

Where, $k_f$ and 1/n are empirical constants indicating adsorption capacity and intensity, respectively. These models help determine the capacity and efficiency of *Citrus reticulata* peel in adsorbing methylene blue and provide insight into the nature of the adsorption process, whether it is physical or chemical, and whether the biosorbent surface is homogenous or heterogeneous.

## MATERIALS AND METHODOLOGY

### Materials

Fresh *Citrus reticulata* (mandarin orange) peels were collected from local markets. The peels were thoroughly washed with distilled water to remove dirt and surface impurities, then air-dried for 72 hours, followed by oven drying (Universal Oven UF55, Memmert, US) at 60°C for 24 hours to ensure complete removal of moisture. Approximately 50 g of the dried peels were ground using a mechanical grinder (Waring 39 Laboratory Blender, USA) and sieved (Retsch, Germany) to obtain a uniform particle size of approximately 250 µm. The biosorbent was stored in an airtight container at room temperature until further use. Methylene blue (MB), a cationic dye of analytical grade, was used as the adsorbate. A stock solution of 1000 mg/L was prepared by dissolving 1000 mg of MB in 1 Liter of distilled water. Working solutions of various concentrations (10–100 mg/L) were obtained by serial dilution of the stock solution.

### Characterization and Batch Adsorption Experiments

The surface morphology of the biosorbent was examined using scanning electron microscopy (SEC SNE-3000MS Table Top SEM). All experiments were carried out in batch mode to investigate the effects of various operational parameters on dye removal efficiency. The adsorption experiments were conducted in 250 mL Erlenmeyer flasks containing 100 mL of MB solution at specified conditions. The flasks were agitated in a temperature-controlled orbital shaker at 150 rpm. To assess the impact of initial pH on MB adsorption, solutions with a constant dye concentration (100 mg/L) were adjusted to different pH values (3–10) using 0.1 M HCl or 0.1 M NaOH. The pH was measured using a calibrated digital pH meter. Biosorbent doses ranging from 0.2 to 2.0 g/100 mL were tested to determine the optimal amount required for maximum dye removal. To investigate the adsorption kinetics, the contact time was varied from 5 to 180 minutes. Samples were collected at predetermined intervals and analyzed for residual dye concentration. The effect of initial dye concentration was studied by varying MB concentrations from 10 to 100 mg/L while keeping the biosorbent dose and pH constant. This experiment helped assess the biosorbent's capacity and the nature of the adsorption process.

The concentration of methylene blue in the filtrate was measured using a UV-Vis spectrophotometer at the maximum absorbance wavelength of 664 nm. The percentage removal and adsorption capacity (qe) were calculated using the following equations:

$$\% \, Removal = \frac{C_0 - C_e}{C_0} \times 100\%$$

$$q_e = (C_0 - C_e)\frac{V}{M}$$

Where, C0 and Ce are the initial and equilibrium concentrations (mg/L), respectively; V is the volume of the solution (L); and M is the mass of biosorbent used (g).

### Isoterm Modelling

Equilibrium adsorption data were fitted to the Langmuir and Freundlich isotherm models using non-linear regression analysis. Model performance was evaluated using the correlation coefficient ($R^2$) to determine the best-fitting isotherm [7].

## RESULTS AND DISCUSSION

### Surface Morphology

Scanning electron microscopy (SEM) revealed a rough, porous surface morphology of the *Citrus reticulata* peel powder, providing ample surface area and active sites for dye adsorption. After methylene blue adsorption, SEM images (Figure 1) showed smoother surfaces with dye molecules visibly embedded, indicating successful uptake.

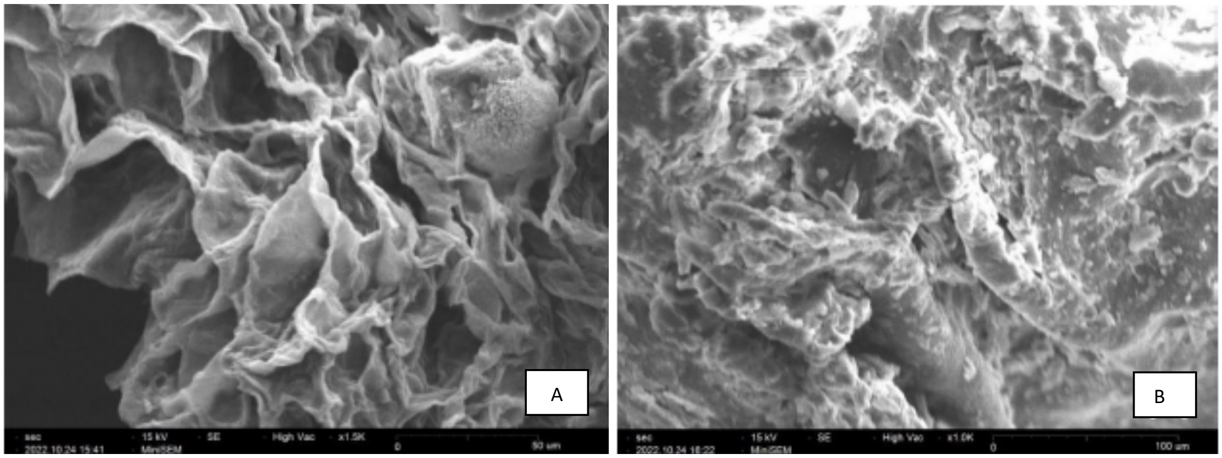


**Figure 1.** SEM Micrograph of *Citrus reticulata* biosorbent before (A) and after (B) adsorption take place at 250x 1000x magnification

### Effect of pH

The adsorption of methylene blue was significantly influenced by pH, with maximum removal observed at pH 9 (Figure 2). At lower pH values, the biosorbent surface becomes protonated, reducing the attraction between positively charged dye ions and the adsorbent. As the pH increases, deprotonation enhances electrostatic interactions with the cationic dye. This trend aligns with findings from other biosorption studies using citrus-derived biomass [4].

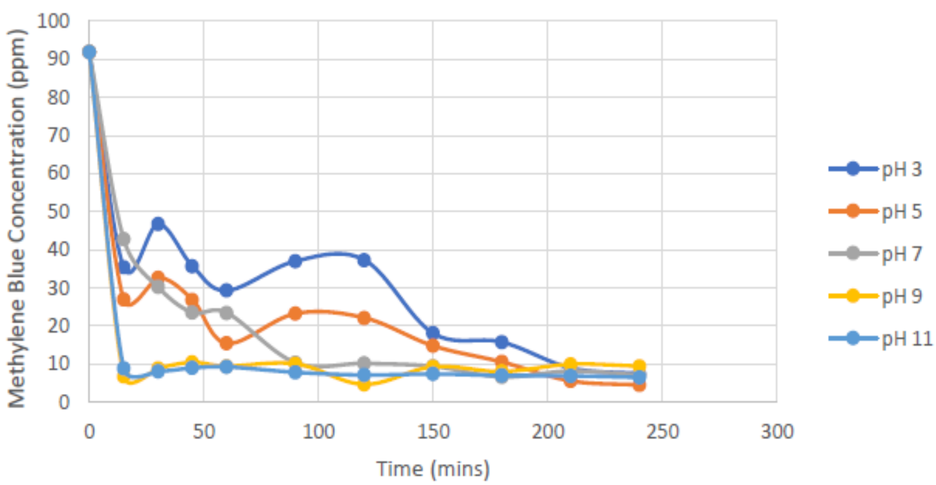


**Figure 2.** Effect of different pH of methylene blue on the adsorption of *Citrus reticulata*

### Effect of Sorbent Dosage

The dye removal efficiency increased with increasing biosorbent dosage (Figure 3), reaching an optimal value at 0.5 g/100 mL. This improvement is attributed to the greater availability of adsorption sites. However, beyond the optimum dose, the removal efficiency plateaued, likely due to particle aggregation or saturation of active sites [8].

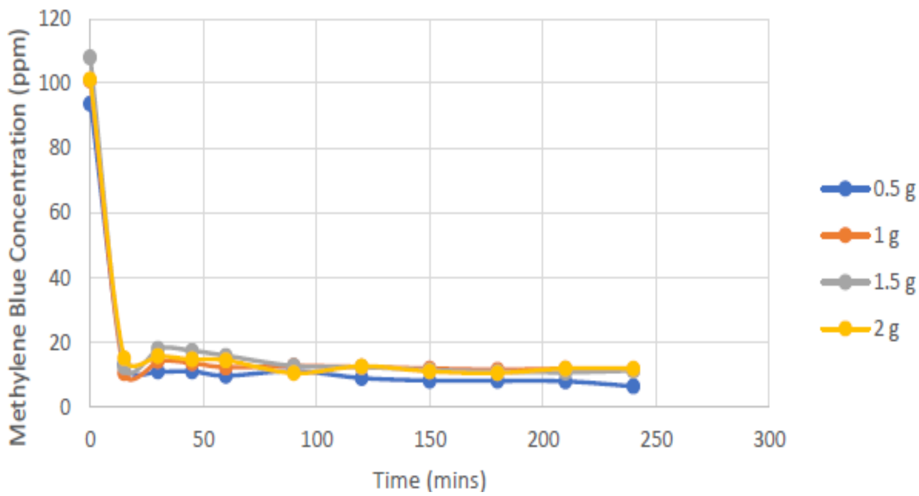


**Figure 3.** Effect of sorbent dosage on the adsorption of *Citrus reticulata*

### Effect of Contact Time

Rapid adsorption capacity (qe) occurred within the first 30 minutes, followed by a slower rate until equilibrium was reached at approximately 50 minutes (Figure 4). The initial rapid phase is due to abundant active sites, while the slower phase reflects the saturation of available sites and intraparticle diffusion limitations [9]. This biphasic behavior is characteristic of most biosorption processes.

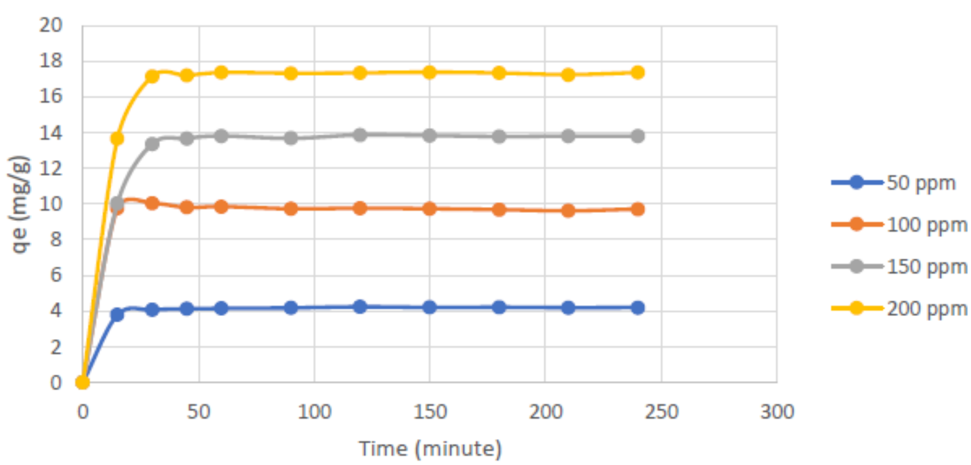


**Figure 4.** Effect of contact time on the adsorption of *Citrus reticulata*

### Effect of Initial Dye Concentration

As the initial concentration of methylene blue increased, the adsorption capacity (qe) also increased, indicating that higher dye concentrations provide a greater driving force for mass transfer (Figure 5) [9]. However, the percentage removal decreased slightly at very high concentrations due to the fixed number of active sites on the biosorbent surface.

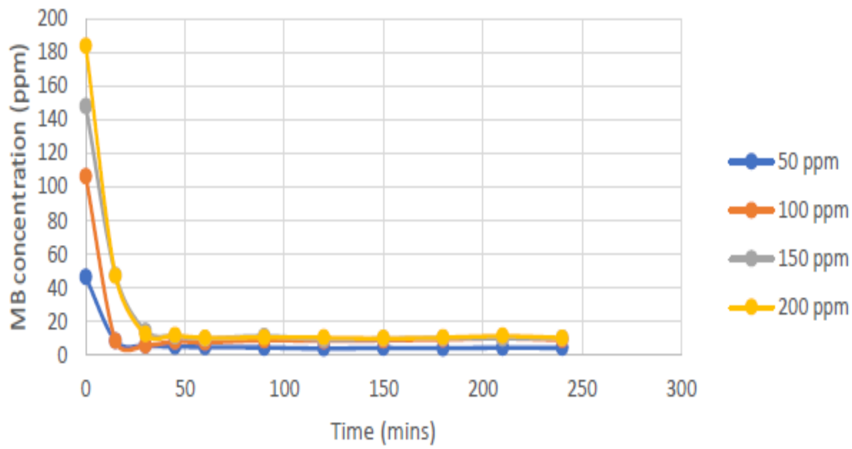


**Figure 5.** Effect of initial concentration on the adsorption of *Citrus reticulata*

## Adsorption Isoterms

Equilibrium data were fitted to Langmuir and Freundlich models to elucidate the adsorption mechanism. It was found that Langmuir Isotherm provided the best fit, with a high correlation coefficient (R2=0.9577), suggesting monolayer adsorption on a homogenous surface. The maximum adsorption capacity (qmax) was estimated at 19.84 mg/g. For Freundlich Isotherm, although it also showed a reasonable fit, the lower R2=0.903 value compared to Langmuir implies a less heterogeneous adsorption process. The Freundlich constant kf<1 indicated favorable adsorption conditions.

**Table 1.** Constants of Langmuir and Freundlich Isotherms for Biosorption of Methylene Blue Dye

| Dye | Langmuir Constants | | | Freundlich Constants | | |
|---|---|---|---|---|---|---|
| | *qmax* (mg/g) | *b* (1/mg) | *R2* | *kf* | *nf* | *R2* |
| Methylene blue | 19.84 | 0.065 | 0.9577 | 0.45 | 0.653 | 0.903 |

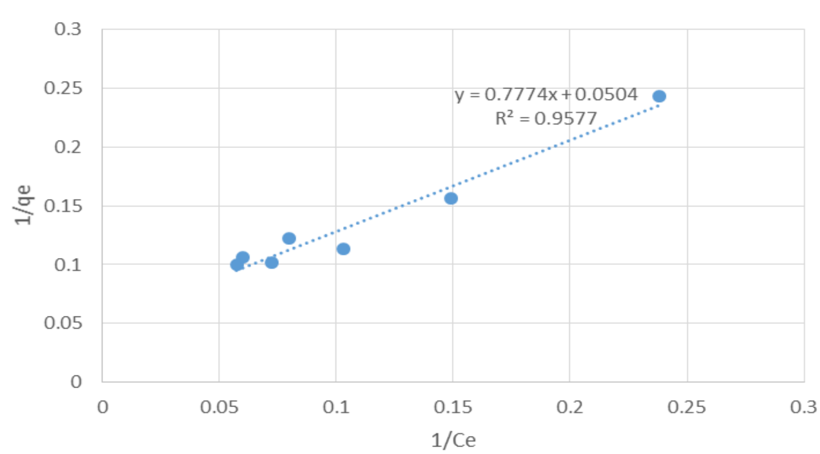


**Figure 6.** Langmuir Isotherm adsorption by *Citrus reticulata* Peel

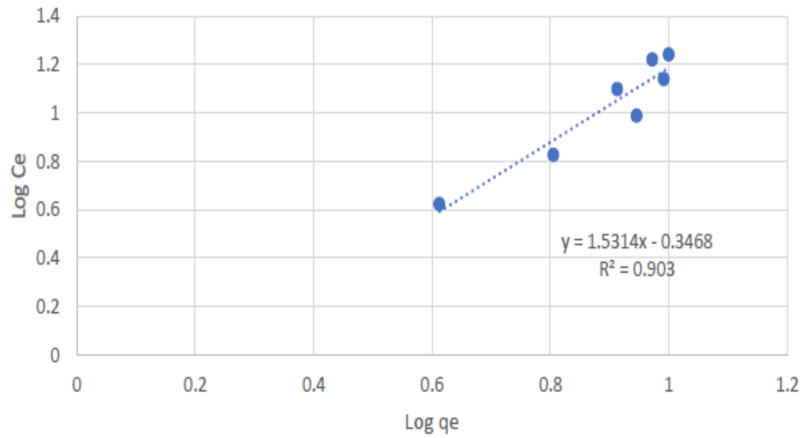


**Figure 7.** Freundlich Isotherm adsorption by *Citrus reticulata* Peel

## CONCLUSION

This study investigated the adsorption behavior of methylene blue (MB) dye onto a biosorbent using batch equilibrium experiments. The adsorption isotherms were analyzed using both Langmuir and Freundlich models. The results revealed that the adsorption capacity increased with higher initial dye concentrations, indicating favorable adsorption conditions. The experimental data showed a strong correlation with the Langmuir isotherm model, suggesting monolayer adsorption onto a homogeneous surface. The calculated Langmuir constants indicated a high adsorption capacity and favorable sorption, supported by a high correlation coefficient. Although the Freundlich model also provided a reasonable fit, its lower $R^2$ value implied that the surface of the biosorbent may be more uniform than heterogeneous [10]. The maximum adsorption capacity (qmax) determined from the Langmuir model further supports the potential of the biosorbent as an efficient material for dye removal from aqueous solutions.


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## CONFLICTS OF INTEREST

The authors declare no conflict of interest.

## REFERENCES


[1] Samsami, S., Mohamadi, M., Sarrafzadeh, M.H., Rene, E.R. and Firoozbahr, M. (2020). Recent advances in the treatment of dye-containing wastewater from textile industries: Overview and perspectives. *Process Safety and Environmental Protection*, 143, pp. 138–163. https://doi.org/10.1016/j.psep.2020.05.034

[2] Al-Tohamy, R., Ali, S.S., Li, F., Okasha, K.M., Mahmoud, Y.A.G., Elsamahy, T., Jiao, H., Fu, Y. and Sun, J., (2022). A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety. *Ecotoxicology and Environmental Safety*, 231, pp. 113160. https://doi.org/10.1016/j.ecoenv.2021.113160

[3] Pavan, F. A., Gushikem, Y., Mazzocato, A. C., Dias, S. L. P., & Lima, E. C. (2007). Statistical design of experiments as a tool for optimizing the batch conditions to methylene blue biosorption on yellow passion fruit and mandarin peels. Dyes and Pigments, 72(2), 256–266. https://doi.org/10.1016/j.dyepig.2005.09.001

[4] Pathania, D., Sharma, S., & Singh, P. (2017). Removal of methylene blue by adsorption onto ZnO/chitosan

nanocomposite: Kinetics, equilibrium and thermodynamic studies. International Journal of Biological Macromolecules, 87, 295–302.

[5] Ofomaja, A. E., Naidoo, E. B., & Modise, S. J. (2007). Removal of copper (II) from aqueous solution by pine and base modified pine cone powder as biosorbent. Journal of Hazardous Materials, 135(1–3), 280–295.

[6] Kumar, K. V., Ramamurthi, V., & Sivanesan, S. (2010). Modeling the mechanism involved during the sorption of methylene blue onto fly ash. Journal of Colloid and Interface Science, 284(1), 14–21. https://doi.org/10.1016/j.jcis.2004.09.063

[7] Foo, K. Y., & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. Chemical Engineering Journal, 156(1), 2–10. https://doi.org/10.1016/j.cej.2009.09.013

[8] Deniz, F., & Tezel Ersanli, E. (2022). A novel biowaste-based biosorbent material for effective purification of methylene blue from water environment. International Journal of Phytoremediation, 24(12), 1243–1250. https://doi.org/10.1080/15226514.2021.2025039

[9] Leyva-Ramos, R., Salazar-Rábago, J. J., & Ocampo-Pérez, R. (2021). A novel intraparticle mass transfer model for the biosorption rate of methylene blue on white pine (Pinus durangensis) sawdust. Diffusion-permeation. Chemical Engineering Research and Design, 172, 43–52. https://doi.org/10.1016/j.cherd.2021.05.029

[10] Liu, X., Zhao, Y., Yu, H., Li, W., & Xu, H. (2021). Surfactant adsorption isotherms: A review. ACS Omega, 6(46), 31110–31125.