Journal of the Turkish Chemical Society Section A: Chemistry

Turkish Chemical Society

Calcined Eggshell for the Removal of Victoria Blue R Dye from Wastewater Medium by Adsorption

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Abstract: In this study, the use of calcined eggshell (CE) as an adsorbent in removing Victoria Blue R (VBR) dyestuff from the solution medium was investigated. For this purpose, pH, interaction time, adsorbate concentration, amount of adsorbent, and salt effect parameters were studied to determine the appropriate adsorption conditions. The highest adsorption yield was obtained at pH 2, 2.0 g/L adsorbent, and a stirring time of 5 minutes. 97% of the dye was removed under optimum adsorption conditions. The results obtained from the experimental studies showed that the adsorption mechanism is compatible with the pseudo-second-order kinetic model and the Langmuir isotherm model. SEM and IR analysis were performed for the characterization of CE.

Keywords: Textile dye, calcined eggshell, water treatment, wastewater, adsorption, Victoria Blue R.

Submitted: June 29, 2020. **Accepted:** November 09, 2020.

Cite this: Tosun Satır İ, Erol K. Calcined Eggshell for the Removal of Victoria Blue R Dye from Wastewater Medium by Adsorption. JOTCSA. 2021;8(1):31–40.

DOI: https://doi.org/10.18596/jotcsa.760083.

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INTRODUCTION

Synthetic dyes used in various industrial applications spread to the environment as a result of industrial activities (1). More than half of the dyes used in the textile industry disappear after dyeing and approximately 10 - 15% of the dyes are uptake with liquids. (2). Dyes are synthetic aromatic compounds widely used in textile industries (3,4). It is known that these dyes have mutagenic and carcinogenic effects for aqueous systems and human life. It has also known that some triphenylmethane dyes cause tumoral growth in some fish species (5-8). Also, triphenylmethane dyes have a strong coloring feature and reduce the transparency of the water and gaseous solubility in water (9). Fluids from the paint production industry have higher chemical and biochemical oxygen demand and are significantly colorful (3). As this situation poses a serious risk to people and living organisms in the water, developing an effective method to get away these chemicals from the wastewater is becoming essential.

In order to remove triphenylmethane dyes or contaminants from wastewater; there are many methods, including adsorption, flocculation, electrochemical applications, photo-oxidation, and photocatalytic techniques (10-16). Biosorption is the kind of adsorption used as a biomass adsorbent, it has been widely demanded in recent years (17, 18). Victoria Blue R (VBR) is an essential member of the triphenylmethane family of dyes and is extensively used in the industry (19). The removal of the carcinogenic or mutagenic dye from wastewater is of great importance on the environment and human health. Various adsorbents have been used from past to present to remove dye from wastewaters (20-23). One of the most commonly used is activated carbon (24,25). However, the regeneration of this material is due to the prolongation of processing times and additional costs. For this, it is necessary to develop alternative disposable adsorbents with no economic value. In line with this idea, eggshell as an agricultural waste has been preferred because it is no-cost and harmless to the environment. The high percentage of calcium carbonate in the eggshell makes it an effective adsorbent (26).

Within the scope of this work to remove the VBR paint from wastewaters, the calcined eggshell powder was used. It has been studied in both continuous and batch systems, and optimum adsorption conditions (pH, contact time, dye concentration, adsorbent dose, temperature, ionic strength) were provided.

EXPERIMENTAL SECTION

Preparation of Calcinated Eggshells

Eggshells purchased from a local market were first washed ultra-distilled water, then dried in an oven at 60 °C. Eggshells were calcined in the ash oven at 900 °C. After calcination, the adsorbent was ground with a laboratory grinder and sieved through a 150 µm sieve.

Instrumentation

After adsorption, the dye concentration remaining in the solution was measured using a Thermo Genesys 10S UV-VIS spectrophotometer at a wavelength of 615 nm. The surface morphology of CE was examined using Scanning Electron Microscopy (SEM); Carl Zeiss AG - EVO® 50 Series, Germany. With the help of double-sided carbon tape, CE was placed on the SEM sample holder surface. It was then coated with a thin layer of gold under vacuum and examined for surface morphology. The functional groups on the surface structure of CE were analyzed using a Fourier Transform Infrared Spectrometer (FTIR) (Thermo Nicolet iS10 FTIR Spectrometer, USA).

Adsorption Studies

The uptake of VBR dye from aqueous solutions with CE was investigated. To provide maximum removal, the effects of parameters such as adsorbent amount, contact time, pH, temperature, and ionic strength on adsorption capacity were investigated. The obtained data were evaluated with some kinetic and isotherm model parameters were calculated. In order to investigate the effect of pH on adsorption capacity, the pH of the dye solution was changed between 5-10, and adsorption capacity for CE was investigated. 50 mL of the dye solution at a concentration of 100 mg/L was treated with 0.1 g of adsorbent. The adsorbent amount was studied in the range of 0.02 to 0.3 g / 50 mL VBR dye at pH 9.0. The effect of contact time on adsorption capacity was investigated at 3 various temperatures (20, 30, and 40 °C) in the range of 5-90 minutes.
Adsorption capacity and adsorption yield (%) were calculated by the following equations:

$$q_e = \frac{V\left(C_i - C_e\right)}{m} \tag{1}$$

$$Adsorption\ yield\,(\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

where
q_e : Adsorption Capacity (mg/g)
C_i : Initial adsorbate concentration (mg/L)
C_e : Equilibrium adsorbate concentration (mg/L)
V : The volume of dye solution (L)
m : Amount of adsorbent (g)

RESULTS AND DISCUSSION

Characterization of Adsorbent

In the SEM micrograph of CE before adsorption (Fig.1a), a porous and coarse structure was observed, whereas after the adsorption (Fig. 1b), the porous structure became plate-like and the coarse appearance disappeared. This was interpreted as VBR adhering to the adsorbent surface and altering surface morphology.

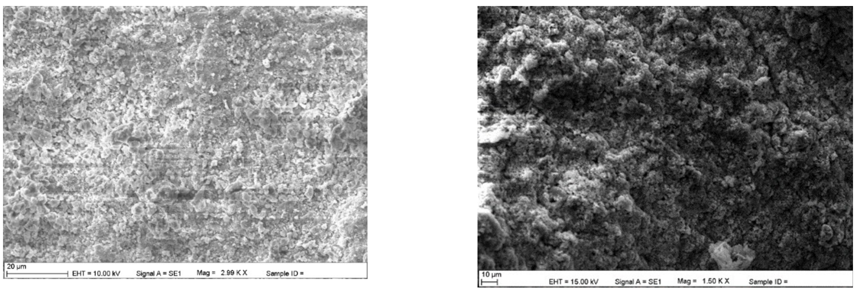

Figure 1: SEM pictogram a)before adsorption, b) after adsorption.

FTIR spectroscopy was performed in the range of 400–4000 cm^{-1} to study the biosorption of VBR on CE. On the FTIR spectrum of CE the peaks at 1403 and 869 cm^{-1} belong to the CO_3^{2-} anion (27).

Effect of pH

Within the scope of the study, firstly, the pH point where optimum adsorption capacity is optimum was investigated. Since VBR dye was dissolved in acidic pH regions, it was studied in regions higher than pH 5. Due to the possibility of interaction with the electron density regions of VBR, the pH was not studied at points higher than 10. As can be seen from the figure, while the adsorption capacity increased in the range of pH 5-8, no significant increase was observed in the range of pH 8-10. According to these results, the optimum pH point was chosen as 9. Furthermore, considering the high calcium carbonate content of the eggshell, a primary point of pH 9 is considered to be an optimal choice.

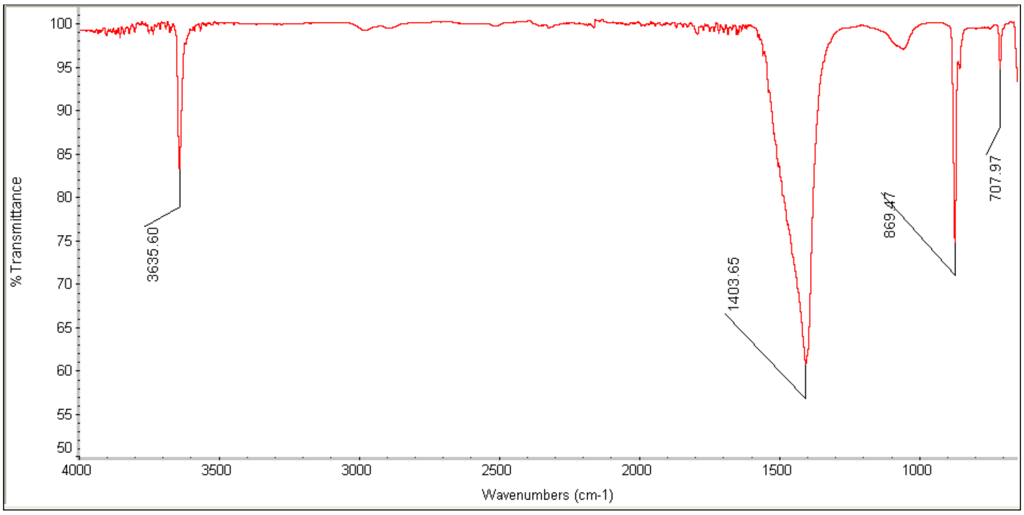

Figure 2: FT-IR Spectrum of calcinated eggshell.

Effect of Adsorbent Amount

To optimize adsorbent amount, the adsorbent amount of 0.4-0.6 g was investigated (Figure 3). A very high extraction rate of 94% was achieved, even at an adsorbent amount of 0.4 g. In the adsorbent amount higher than 3.0 g; a 100% removal was obtained.

Interaction Time

As seen in Figure 4, the effect of the interaction time was examined at 3 different temperatures (20, 30, 40 °C) in the range of 5-90 minutes. The adsorption capacity values remained almost constant when the interaction time was increased from 5 minutes to 90 minutes. q value showed a very low decrease from 26 to 25 with increasing temperature. Optimum interaction time was determined as 5 minutes.

Adsorption Kinetics

The adsorption kinetics is a theoretical basis that determines the time required to establish an adsorption equilibrium. Many kinetic models have been developed to determine the mechanisms of adsorption, such as mass transfer and chemical reaction. The most common kinetic models in the literature are the pseudo-first-order kinetic model (Eq. 2) proposed by Lagergren (28) is the pseudo-second-order kinetic model (Eq. 3) proposed by Ho (29) and the interparticle diffusion equation model for Weber-Morris's (30) mass transfer mechanism (Eq. 4). The equations of kinetic models are as follows:

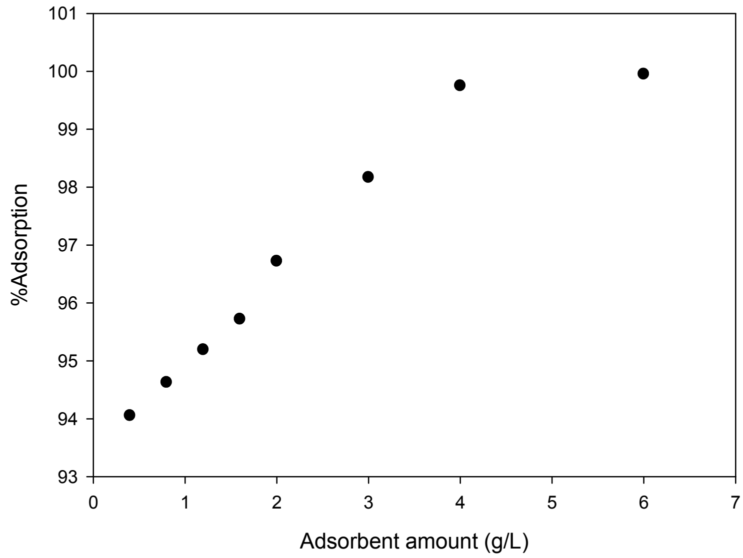

Figure 4: The effect of adsorbent amount on adsorption yield.

In this study, time-dependent data in the adsorption of calcined eggshell and VBR dye were evaluated by pseudo-first-order and pseudo-second-order kinetic models and intra-particle diffusion models. Some constants and r^2 values of the models are given in Table 1.

According to the results obtained from pseudo-first-order kinetic model studies; r^2 values (Table 1) are in the range of 0.959 - 0.997. According to the results obtained, it showed that the change was linear. But, q_e values calculated using y-intercept did not correspond to values obtained with experimental data. These results showed that the adsorption process of the VBR dye on the calcined eggshell did not occur with the first-degree reaction.

When r^2 values (Table 1) of dye adsorption at three different temperatures were examined, it was seen that adsorption was compatible with the pseudo-second-order kinetic model at all temperatures (Fig. 5). Also, the calculated q values were in the acceptable range. As a result, it was determined that the adsorption of the dye onto the calcined eggshell was suitable for the pseudo-second-order kinetic model.

Pseudo-First-Order

$$q_t = q_e\left(1 - \exp^{-k1}\right) \quad (3)$$

Pseudo-Second-Order

$$q_e = \left(\frac{k_2 q_e^2 t}{1 + k_2 q_e t}\right) \quad (4)$$

Weber-Morris's mass transfer mechanism

$$q_t = k_p t^{1/2} + C \quad (5)$$

where:

q_e	Adsorption capacity at equilibrium (mg/g)
q_t	Adsorption capacity at different times (t) (mg/g)
k_1	Pseudo-first-order equilibrium rate constant (1/min)
k_2	Pseudo-second-order equilibrium rate constant (g/mg. min)
k_p	Intra-particle diffusion constant (g/mg. $min^{1/2}$)
C	constant for any experiment (mg/g).

,

Table 1. Kinetic parameters for the adsorption of VBR dye onto CE.

Temperature	Pseudo–first–order			Pseudo–second–order			Intraparticle diffusion		
	K_1 (min^{-1})	q_e (mg g-1)	R^2 (g mg^{-1} min^{-1})	k_2	q_e (mg g^{-1})	R^2	k_p (mg g^{-1} min$^{1/2}$)	C (mg g^{-1})	R^2
20 °C	$6.69\text{x}10^{-2}$	0.470	0.959	$2.76\text{x}10^{1}$	27.020	0.999	0.047	26.372	0.935
30 °C	$5.50\text{x}10^{-2}$	0.364	0.989	$3.01\text{x}10^{-1}$	25.641	0.999	0.043	25.135	0.938
40 °C	$5.10\text{x}10^{-2}$	0.324	0.997	$3.08\text{x}10^{-1}$	25.641	0.999	0.040	25.071	0.961

Table 2 Isotherm model parameters for the adsorption of VBR dye onto CE.

Temperature	Langmuir				Freundlich			Dubinin–Radushkevich (D–R)			
°C	q_{max} (mol g^{-1})	K_L (L mol^{-1})	r^2	R_L	n	K_F (L g^{-1})	r^2	q_m (mol g^{1})	β (mol^2 kJ^2)	r^2	E (kJ mol^{-1})
20	100	$58.8\text{x}10^{-2}$	0.919	0.99	1.052	63.68	0.964	50.95	$5.645\text{x}10^{-8}$	0.959	$29.76\text{x}10^{2}$
30	140	$87.5\text{x}10^{-2}$	0.917	0.99	1.584	51.62	0.912	31.75	$1.663\text{x}10^{-8}$	0.688	$54.83\text{x}10^{2}$
40	140	$87.5\text{x}10^{-2}$	0.937	0.99	1.675	53.96	0.969	34.32	$1.585\text{x}10^{-8}$	0.810	$56.16\text{x}10^{2}$

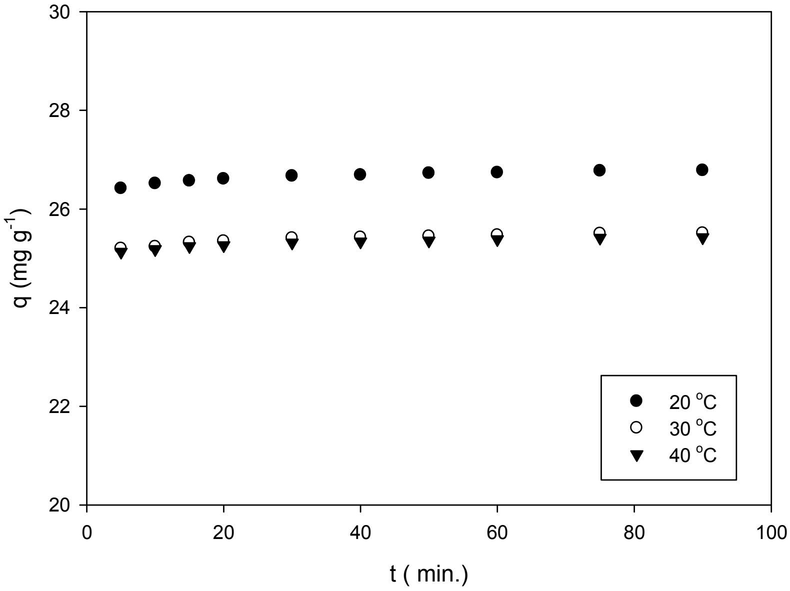

Figure 5: The effect of interaction time and temperature on adsorption yield.

Finally, experimental data was applied to the intraparticle diffusion model. According to the results obtained, it was found that this model does not adapt to the adsorption of the VBR dye on calcined eggshells.

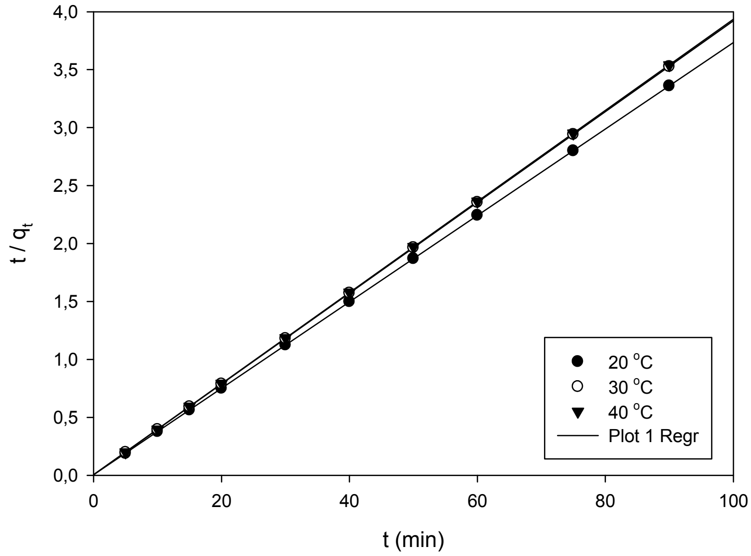

Figure 6: Pseudo-Second-order kinetic graphics.

Adsorption Isotherms

Adsorption in solution phase; temperature depends on concentration when adsorbent and adsorbate are kept constant. In this case, the equation showing the correlation of the amount of a substance bound to the surface at a constant temperature with the concentration of that substance in solution is called adsorption isotherm. The most common isotherms in practice are

Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherms.

According to the Langmuir isotherm model (31), when a molecule is adsorbed to the surface, no more adsorption occurs in the same region. Therefore, the Langmuir equation is valid only for a single layer coating formed by adsorption of a single molecule on a completely homogeneous surface. Langmuir equation;

$$\frac{1}{q_e}=\frac{1}{q_{max}}+\left(\frac{1}{q_{max}K_L}\right)\times\frac{1}{C_e} \quad (6)$$

is calculated by equation (6).

According to the Freundlich isotherm model (32), the adsorption zones on the surface of an adsorbent are heterogeneous. The equation of this isotherm model is expressed as follows.

$$\ln q_e=\ln K_F+\frac{1}{n}\ln C_e \quad (7)$$

q_e : Amount of substance adsorbed in equilibrium (mg/g)
q_{max} : Max. single layer adsorption capacity (mg/g)
C_e : Amount of matter remaining without adsorption in equilibrium (mg/L)
K_F : Freundlich isotherm constant
K_L : Langmuir isotherm constant
ε : Polanyi potential
β : The activity coefficient related to biosorption energy

The D-R isotherm model (33) is used to understand whether adsorption occurring on heterogeneous surfaces is physical or chemical. D-R isotherm model equation:

$$\ln q_e=\ln q_m-\beta\epsilon^2 \quad (8)$$

In this study, the results obtained in equilibrium for the adsorption of VBR dyes to the CE surface were analyzed according to the Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models, respectively. Constant values and r^2 values of all isotherm models are given in Table 2.

When the r^2 values of the adsorption data in Table 2 are compared, it is seen that the Freundlich isotherm model (Fig. 7) is the most suitable model for VBR adsorption.

The value of n appears to be higher than 1 for all 3 temperatures. It shows that the adsorption mechanism occurs voluntarily.

Salt Effect

In order to investigate the effect of ionic strength on adsorption capacity, dye solutions containing NaCl salt with concentrations ranging from 0.01 to 0.4 mol.L^{-1} were prepared. The prepared solutions were mixed with the adsorbent during a 5 minute equilibrium period. The data obtained from the experiment are given in Fig.8.

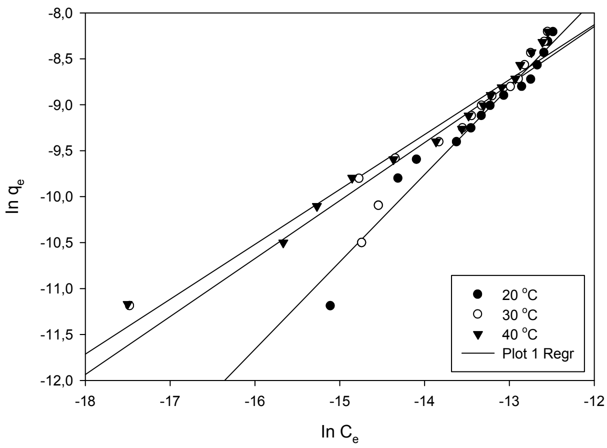

Figure 7: Freundlich isotherm graphics.

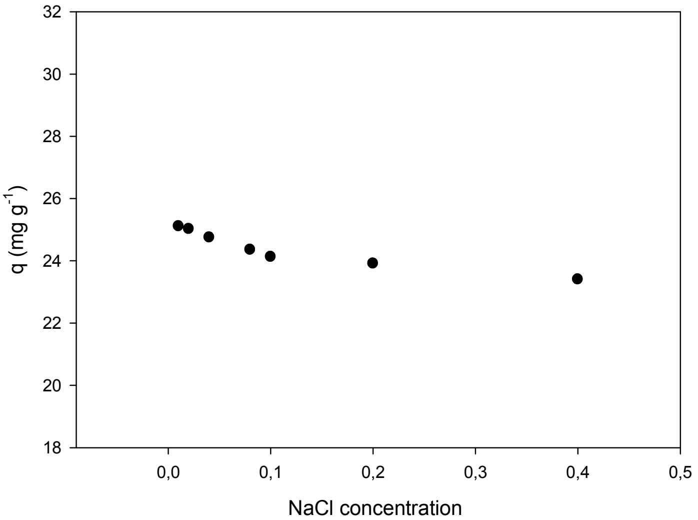

Figure 8: Salt effect on adsorption.

As it is understood from the figure, the increase of the concentration of salt in the medium, a small amount of adsorption capacity has been decreased. This situation indicates that ionic strength does not have a significant effect on the salt concentration range examined with calcined eggshell and VBR adsorption.

Real wastewater

The removal of the VBR dyestuff from the real wastewater environment was investigated in optimum conditions obtained by experimental studies. For this purpose, VBR dyestuff was added to the wastewater taken from the outlet water of a factory. In the adsorption study with real wastewater under optimum experimental conditions, 73.52% removal was observed. This value is very close to the efficiency obtained with synthetic solutions. This situation indicates that other components in the wastewater environment are not in competition with the VBR dyestuff to bind to the active sites on the adsorbent surface under the conditions under study. Thus, it has been revealed that the VBR dyestuff in wastewater can be removed from the environment with a small decrease in the adsorption efficiency with calcined eggshells.

CONCLUSION

In this study, the optimum pH value was determined as 6.0. The optimum pH value determined is also close to the initial pH of the dye solution (original dye solution pH = 5.62). Adsorption equilibrium has been established in a short time like 5 minutes. The adsorption process is best explained by the Freundlich isotherm model and the pseudo-second-order kinetic model. 73.52% eggshell is thought to be a very effective adsorbent due to its abundance and waste in nature and high adsorption capacity. Removal was achieved under optimum adsorption conditions in a real wastewater environment.

ACKNOWLEDGMENTS

This study was supported by the Scientific Research Projects Department of Hitit University (Project no: FEF01.13.009)

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