MONTMORILLONITE K10 AND NaK10 AS BIFUNCTIONAL MATERIALS: SCAVENGERS OF FORMALDEHYDE FROM UREA-FORMALDEHYDE RESINS AND METHYLENE BLUE IN AQUEOUS MEDIA

Mirjana Ristić[1], Suzana Samaržija-Jovanović[1], Tijana Jovanović[2], Marija Krstić[3], Vojislav Jovanović[1], Gordana Marković[4], Milena Marinović-Cincović[5]

[1]University of Pristina in Kosovska Mitrovica, Faculty of Sciences and Mathematics, Serbia
[2]University of Niš, Faculty of Sciences and Mathematics, Serbia
[3]University of Novi Sad, Faculty of Technology, Novi Sad, Serbia
[4]Tigar, Pirot, Serbia
[5]University of Belgrade, Institute of Nuclear Sciences "Vinča" - Institute of national importance for the Republic of Serbia, Serbia

WHAT WE DID

In this work, the reduction of formaldehyde (FA) from urea-formaldehyde resins (UF) and removed methylene blue (MB) in aqueous media was performed, using clay from the smectite group, one of which is chemically modified (Figure 1a).

MATERIALS AND METHODS

Materials: Urea supplied from Alkaloid (Skopje, Republic of North Macedonia), 35% formaldehyde supplied from Unis (Goražde, Bosnia and Herzegovina), Montmorillonite K10 (220-270m^2/g) (Sigma Aldrich, Germany). Methylene blue dye (Thermo Fisher Scientific, USA). All other materials and solvents used for analytical methods were of analytical grade.

Synthesis of NaK10:
15 g of K10 was weighed and dispersed in 500 cm^{-3} of 1M NaCl. The meat is suspended on a magnetic mixer at 550 rpm for 24 hours. After that, the liquid is decanted, and the montmorillonite is washed off. with water to a negative reaction to Cl$^-$ ions. After that, the NaK10 is dried at 105°C to a constant mass.

Determination of cation exchange capacity (CEC): CEC is a measure of the ability of clay materials to bind or retain exchangeable cations.
The cation exchange capacity was calculated using the following equation (1):

$$CEC = (cxV)/m \qquad (1)$$

c- concentration of MB solution (mol/dm^3), V - volume of added MB solution (dm^3), m-mass of sample (kg)

SEM micrographs: Micrographs of the K10 and NaK10 were taken with a Tescan FE-SEM Mira 3 XMU scanning electron microscope at 20 kV acceleration voltage. Before recording, the samples were steamed with gold on a Polaron SC503, Fisons Instruments (Figure 2).

Synthesis and modification of UF composites: Two samples (UF/K10 and UF/NaK10), were synthesized with formaldehyde to urea (F/U) ratio (0.8) using the same procedure [1].

Determination of free and liberated FA: The hydrolytic stability of the modified UF composites was determined by measuring the concentration of liberated FA of the modified UF composites after acid hydrolysis. The percentage of free and liberated FA was determined using the sulfite method [2, 3].
Sorption experiment: were carried out in batch mode with 50 cm^3 of dye solution (20 ppm) and 500 mg of material, and mixed on a magnetic stirrer. Aliquots are taken at certain periods and the color concentration is determined with a UV-Vis spectrophotometer.
Dye removal was calculated using the following equation (2):

$$R = \frac{C_o - C_e}{C_o} \cdot 100\% \qquad (2)$$

R is removal, C_o is for initial concentration, and C_t is for concentration after time t.

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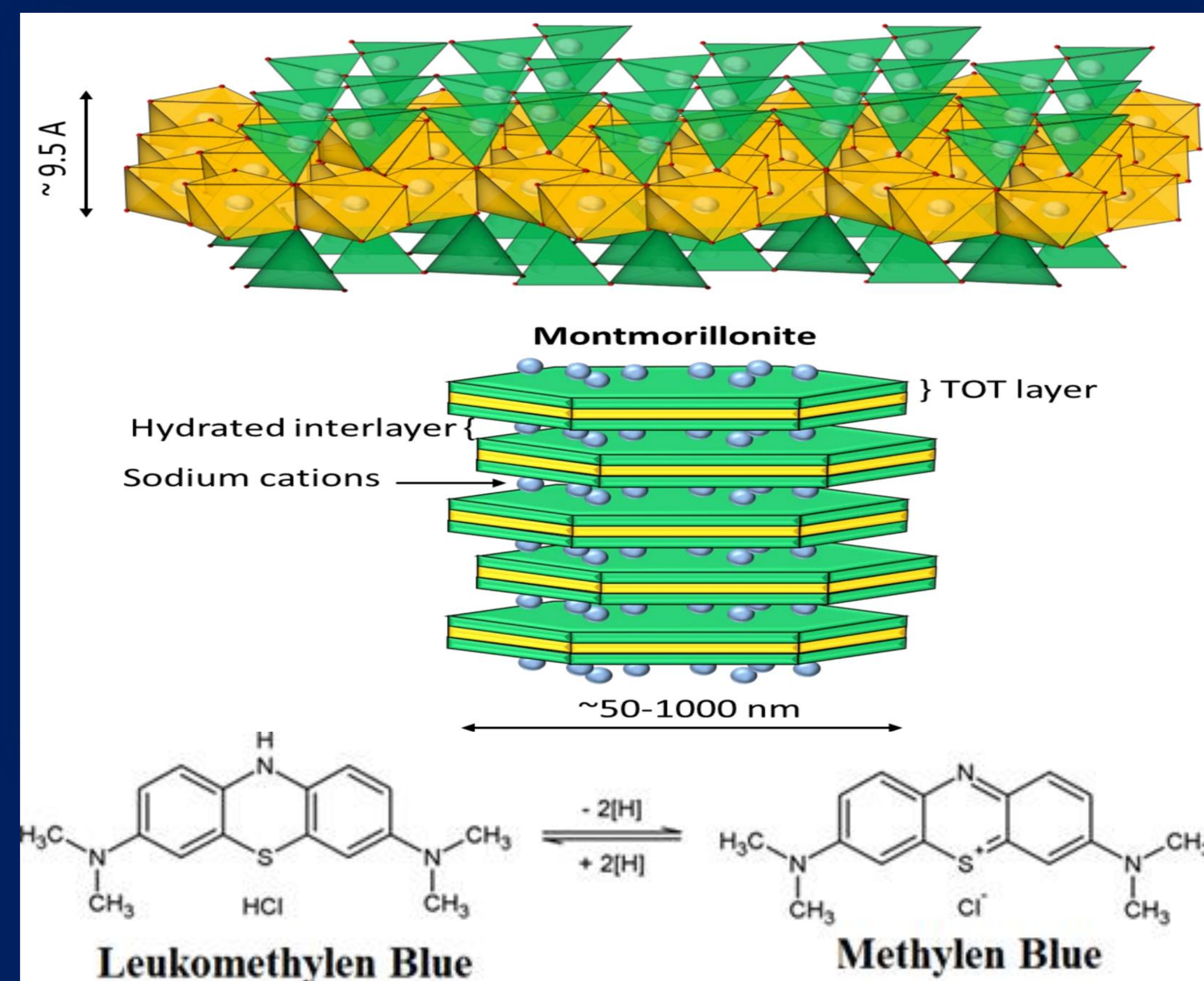

Figure 1*. Structure of a) MMT and b) MB dye*

Table 1. *SSA and CEC of K10 and NaK10*

K10		NaK10	
SSA (m^2/g)	CEC (mol/kg)	SSA (m^2/g)	CEC (mol/kg9
93.5	0.2	74.3	0.14

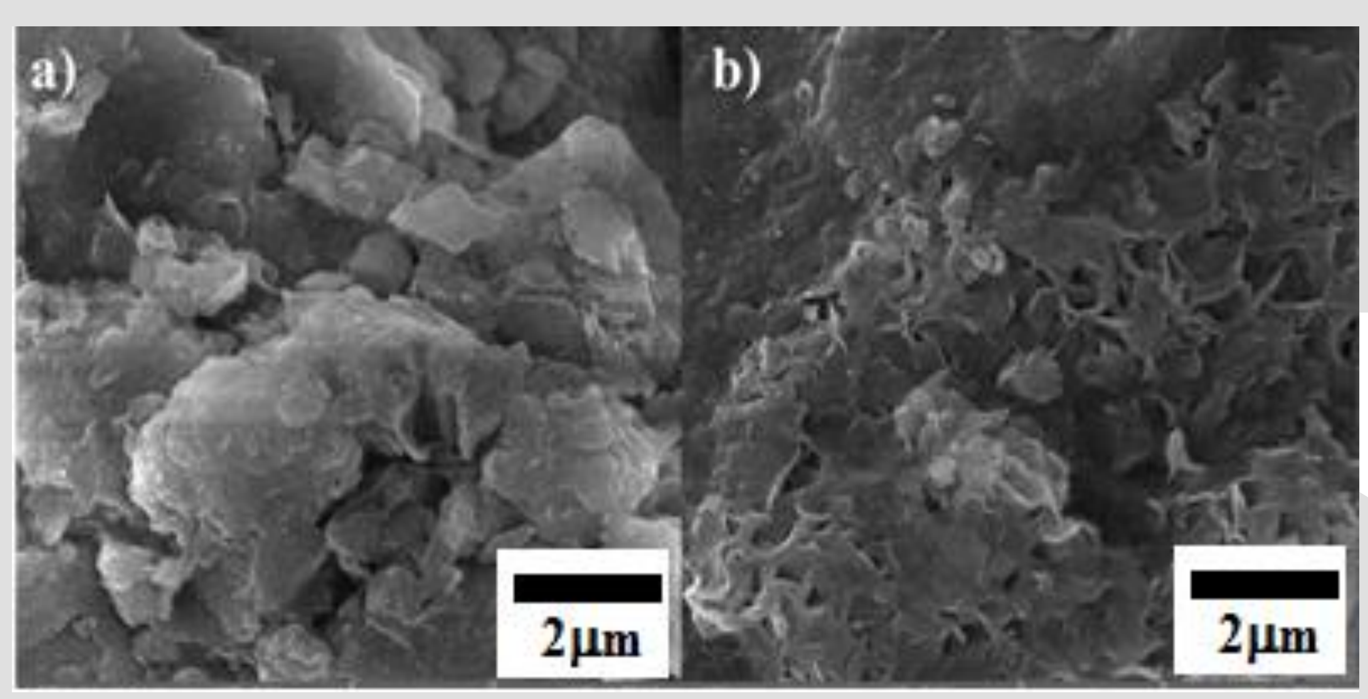

Figure 2*. SEM micrographs of (a) K10, and (b) NaMMT with magnification at 20000x.*

Figure 3*. The ability of montmorillonite to remove MB dye*

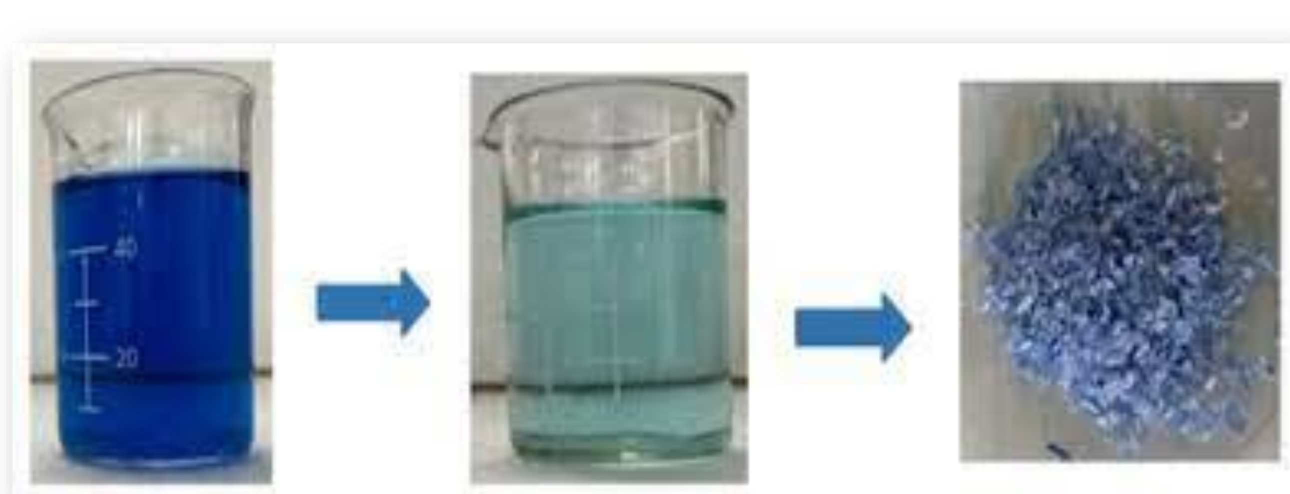

Table 2*. Free and liberated FA in UF/K10 and UF/NaK10*

UF/K10		UF/NaK10	
Free FA (%)	Liberated FA (%)	Free FA (%)	Liberated FA (%)
0.12	2.76	0.12	1.08
R (%)		R (%)	
97.64		98.75	

RESULTS AND DISSCUSION

Due to its physicochemical and sorption properties, clay is material used in environmental protection and water purification. The adsorption behavior of different clays is determined by large SSA, strong adsorption affinity, low permeability, high CEC, high swelling property, and low price [4, 5]. The specific surface area (SSA) of K10 clay is 93.5 m^2/g, and NaK10 is 74.3 m^2/g. The value of CEC for unmodified K10 is 0.2 mol/kg, and for modified NaK10 is 0.14 mol/kg (Table 1). Usually, these clay materials are used as much as natural, but various modifications can improve the adsorption capacity of the clay leading to its wide use in new technologies. In this work, the bifunctionality of K10, and NaK10 was demonstrated. Namely, both clays proved to be excellent catchers of free FA in UF resins, and are also capable of removing the dye MB from the water environment. Figure 2a shows pure K10, it can be seen that it consists of irregularly shaped particles of different sizes. Fluffy particles form agglomerates, forming an aggregate mass and creating a heterogeneous surface morphology. Inorganically modified montmorillonite shows plate-like and slightly rounded shapes of mineral grains. Based on Figure 2b, it can be said that a network of hollows has developed, which affected the percentage of MB dye adsorption (Table 2). Using the disulfite method, it was determined that the percentage of free FA in both resins, (UF/K10, UF/NaK10) is 0.12, which indicates the same ability of the clay (Figure 3), regardless of the chemical modification. Using the same method, after acid hydrolysis, determined that the modified clay UF/NaK10 is hydrolytically more stable (% liberated FA for UF/K10=2.76, and % liberated FA for UF/NaK10=1.08) (Table 2*).* Modified clay NaK10 (0.5g of NaK10, 50 cm^3 of aqueous dye solution, c=20 mg/dm) was also shown to have a slightly better ability to remove MB dye from the water environment, with a value of 98.75%, while the ability of unmodified resin is slightly lower and amounts to 97.64 %, under the same conditions (Table 2*)*

CONCLUSIONS

- ✓ Both resins have the same ability to bind free FA in UF resins, regardless of the chemical modification of one of them.
- ✓ UF/NaK10 resin is hydrolytically more stable.
- ✓ K10 removed 97.64% of MB dye.
- ✓ NaK10 removed 98.75% of MB dye.

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