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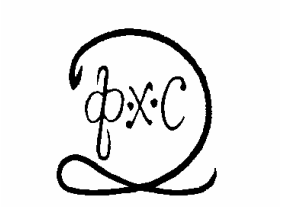

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ALKYLAMMONIUM CLAY BASED NANOCOMPOSITES VS. ALKYLAMMONIUM- MODIFIED LIGNOCELLULOSIC MATERIALS IN ADSORPTION OF CONGO RED

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ABSTRACT
In this study, lignocellulose waste materials and smectite clay were modified into adsorbents with surface free ammonium groups. Poplar waste biomass and brewer's spent grain were chemically modified. Smectite based adsorbents were obtained by intercalation of biopolymer chitosan and hexadecyl trimethylammonium ($HDTMA^+$) cations in smectite structure. The samples were characterized by using X-ray diffraction, elemental analysis and FTIR spectroscopy. The adsorbents were tested for removal of azo dye Congo Red (CR). The concentration of CR was analyzed before and after adsorption test using Thermo Electron Nicolet Evolution 500 UV-VIS spectrophotometer in wavelength range from 250 – 800 nm. It was estimated that adsorption isotherms of CR for all investigated adsorbents showed best fit with Langmuir adsorption model.

INTRODUCTION
During the last decades, the materials with free surface (alkyl)ammonium groups were recognized as promising adsorbents [1, 2] since these groups can electrostatically interact with anionic sites present in numerous pollutants. The industrial and agricultural waste (i.e. lignocellulosic waste) and low-cost clays are in the research focus since these raw materials can be converted to very efficient adsorbents using relatively simple modification methods [2, 3]. In this work, lignocellulosic waste materials and smectite were modified into adsorbents with free surface ammonium groups. The obtained materials were evaluated as adsorbents of anionic synthetic dye Congo Red.

EXPERIMENTAL
Poplar waste biomass (PWB, wood shavings and sawdust), donated by "Hrvatske šume d.o.o." and brewers' spent grain (BSG), provided by "Osijek Brewery d.o.o." were subjected to chemical modification according to the previously described procedure [3]. The samples were denoted as mPWB and mBSG, respectively. The 2 μm fraction of smectite (Bogovina, Serbia) with cation exchange capacity (CEC) of 0.633 mmol g^{-1} was used as a host material for intercalation of chitosan (av. M_W =342,500 g mol^{-1}, Sigma-Aldrich) and hexadecyl trimethylammonium (HDTMA) bromide, Alfa-Aesar Chemical. The common procedure [4] was applied to obtain 2H-S with $HDTMA^+$: CEC ratio 2:1. The previously described procedure [5] was used to obtain a sample with chitosan (C-S).

The synthetic dye –Congo Red (CR), (Carlo Erba) was used as test model pollutant in adsorption tests.

The smectite samples were characterized using a Rigaku SmartLab automatic multipurpose X-ray diffractometer (Cu anode, λ=0.1542 nm), while elemental analysis (Perkin Elmer CHNS/O analyzer, Series II) and FTIR spectroscopy (Cary 630, Agilent Technologies) were used for lignocellulosic samples characterization.

The adsorption isotherms for CR were obtained in a batch system at 25 °C using a thermostated shaker (Memmert WNE14/ SV 1422). The CR concentration after adsorption was estimated by Thermo Electron Nicolet Evolution 500 UV-VIS spectrophotometer at λ_{max}=496 nm. All adsorption experiments were conducted in duplicate, and the mean values were reported.

RESULTS AND DISCUSSION

The XRD spectra of 2H-S and C-S showed the presence of smectite as main mineral (> 90 mass %) with only a small amount of quartz. According to literature data, the obtained d_{001}=2.02 nm and 2.08 nm for C-S and 2H-S, respectively, indicated that interlamellar space of smectite was fulfilled with bi-layer arrangement of chitosan [5] and pseudo-three molecular arrangement of $HDTMA^+$ [4]. These forms of intercalated organic species provide the presence of free ammonium groups [4, 5].

The elemental CHN analysis showed the increase in nitrogen content of both modified lignocellulosic materials compared to unmodified waste materials (from 0.21 to 8.93% and from 3.6 to 10.17% for mPWB and mBSG, respectively), which is in accordance with the literature [2, 3]. FTIR spectra of unmodified and modified lignocellulosic samples revealed the presence of a large number of hydroxyl groups that are, among others, mainly engaged in the adsorption processes. Furthermore, FTIR spectra of mPWB and mBSG showed a shift in vibration frequency of some groups and the appearance of new bands associated with quaternary ammonium groups introduced by modification procedure (quaternisation).

The adsorption isotherms of CR dye on modified lignocellulosic waste materials (mPWB and mBSG) are given in Fig 1a, while adsorption isotherms of CR on smectites based composites (2H-B and C-B) are given in Figure 1b. Equilibrium was reached for shorter times, but 240 min was taken as adsorption time sufficient for all processes to reach adsorption maximum. Adsorption isotherms for mPWB and mBSG showed similar uptake of CR, with q_e ~ 50 mg g^{-1} (Fig 1a), while values of q_e were ~ 100 mg g^{-1} and ~300 mg g^{-1} for C-S and 2H-S, respectively. The superior adsorption properties of 2H-S can be explained by the formation of *pseudo*-tri molecular arrangement of intercalated $HDTMA^+$, providing a high amount of surface available ammonium groups as active adsorption sites.

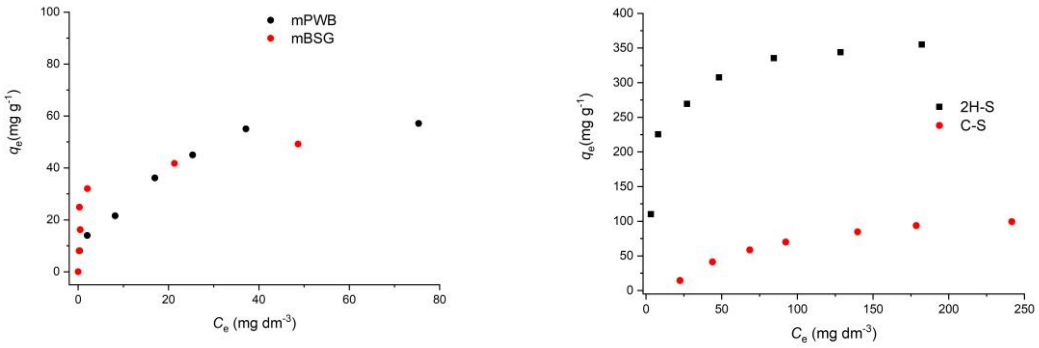

Figure 1. Adsorption isotherms of CR on a) mPWB and mBSG; b)2H-B and C-B. Adsorption conditions: C_0=25, 50, 75, 100, 150, 200 and 250 mg dm^{-3}; m_{ads}= 10 mg of 2H-S and C-S and 150 mg of mPWB and mBSG ; t_{eq}=240 min.

The adsorption data were fitted with Langmuir and Freundlich models, and corresponding constants are given in Table 1.

Table 1. Langmuir and Freundlich parameters

Samples	Freundlich parameters			Langmuir parameters		
	K_F (dm^3g^{-1})	n	R^2	q_{max} ($mg\ g^{-1}$)	K_L ($dm^3\ mg^{-1}$)	R^2
mPWB	12.25	2.65	0.956	70.33	0.069	0.960
mBSG	23.10	5.51	0.904	47.00	1.52	0.917
C-B	5.18	1.81	0.952	154.70	0.0083	0.984
2H-B	127.96	4.81	0.865	357.56	0.1588	0.963

For all investigated adsorbents, the correlation coefficient in the Langmuir model is closer to unity and therefore, can be regarded as the more appropriate model.

CONCLUSION

Adsorbents with free ammonium groups as active sites were tested in batch adsorption study of Congo Red (CR) dye removal. Lignocellulosic waste materials (poplar waste biomass and brewers' spent grain) were chemically modified in order to introduce ammonium groups. The introduction of $-NH_3^+$ groups in lignocellulosic adsorbents was confirmed by CHN analysis and FTIR. The intercalation of chitosan and hexadecyl trimethylammonium ($HDTMA^+$) in smectite structure in smectite based adsorbents was confirmed by XRD analysis. The adsorption processes for all investigated adsorbents could be described by the Langmuir adsorption model. Although HDTMA-smectite had superior adsorption properties toward CR, chemically modified poplar waste biomass, brewers' spent grain as well as chitosan-smectite composite represent a green alternative to conventional alkylammonium-smectites and could be successfully applied in treatment of moderate-loaded effluents.

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