



PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

September 22-26, 2014
Belgrade, Serbia



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PHYSICAL CHEMISTRY 2014

*12th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

*Organized by
The Society of Physical Chemists of
Serbia*

*in co-operation
with_*

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*Boreskov Institute of Catalysis of Siberian Branch of the Russian Academy
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CHITOSAN-SMECTITE BIOINTERFACES VS. ALKYLAMMONIUM-CLAY INTERFACES IN ADSORPTION PROCESS

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ABSTRACT

Two series of chitosan-clay nanocomposites were synthesized using commercial (CLOISITE[®] Na⁺) and Na⁺-enriched Serbian clay from seldom investigated locality Mečji Do. The samples were characterized by X-ray diffraction and intercalation of chitosan into bilayer structures was confirmed for particular chitosan/clay ratio in both series of chitosan-clay nanocomposites. Reactivity of chitosan-smectite biointerfaces vs. alkylammonium-clay interfaces in adsorption process was compared using textile dye Reactive Black 5 (RB5) as adsorbate. Chitosan-clay nanocomposites had similar adsorption uptake, being more than three times higher than adsorption uptake of commercial alkylammonium-clay CLOISITE[®] 30B. The Langmuir adsorption model was found to be appropriate for all investigated adsorbents.

INTRODUCTION

Chitosan-clay nanocomposites are promising materials with organic-inorganic hybrid interfaces [1-4]. Since these materials contain a biopolymer such as chitosan they represent a green alternative to conventional alkylammonium organoclays in their applications, i.e. as adsorbents. The intercalation of chitosan into smectite clay can result in monolayer and/or bilayer arrangements. When bilayer structures are formed some free -NH₃⁺ groups are present in the interlamellar region [1,5] making these materials suitable for adsorption of anionic species, i.e. anionic textile dyes.

In this work series of chitosan-clay nanocomposites with different chitosan loading were synthesized using two smectite clays: commercial (CLOISITE[®] Na⁺) and Na⁺-enriched Serbian clay. The XRD was used to confirm the intercalation of chitosan. Only nanocomposites with bilayered intercalation of chitosan were tested as adsorbents. The adsorption of

anionic dye RB5 on the selected samples was tested and compared with the adsorption on CLOISITE[®] 30B.

EXPERIMENTAL

Materials

Two bentonite clays were used for synthesis of nanocomposites: commercial clay CLOISITE[®] Na⁺ (Southern Clay Products Inc., Texas, USA) and Na⁺-enriched Serbian clay, from locality Mečji Do denoted as KB2, both with particle size <2 μm. High molecular weight chitosan (av. $M_w = 342,500 \text{ g mol}^{-1}$) was supplied by Sigma-Aldrich. Organoclay – CLOISITE[®] 30B (Southern Clay Products, Inc., Texas, USA) was used to compare reactivity of chitosan-smectite biointerfaces vs. alkylammonium-clay interfaces in adsorption process. The synthetic textile dye –RB5, was supplied from Sigma Aldrich, and used for adsorption tests.

Synthesis and characterization of chitosan-clay nanocomposites

Chitosan solutions were prepared by the addition of 20, 40, 80, 160, 400 and 640 mg of chitosan to 1% (v/v) acetic acid and stirred until complete dissolution. After the pH was adjusted to 4.6-5, the chitosan solution was added into 2% clay suspension (0.5 g clay/25 cm³ bidistilled water) at room temperature. The suspension was stirred for 48 hours. The obtained samples were centrifuged and then air-dried at 50 °C and ground to powder. The samples were denoted according to initially added chitosan mass and clay designation. The obtained samples were characterized using powder X-ray diffractometer BRUKER D8-ADVANCE equipped with scintillation detector and copper K_α radiation (40 kV and 30 mA).

Adsorption test

The adsorption of RB5 was performed in a batch system at 25°C using thermostated shaker (Memmert WNE 14 and SV 1422). The initial concentrations of RB5 dye were: 20, 30, 40 and 50 mg dm⁻³. The 0.0100 g of the adsorbents were dispersed in 50.00 cm³ of adsorbate solution and shaken for 1440 min. Equilibrium was reached for shorter times, but 1440 min was taken as adsorption time sufficient for all adsorbents to reach maximum of adsorption. After adsorption, solid and liquid phase were separated by centrifugation. The RB5 concentration was estimated by Thermo Electron Nicolet Evolution 500 UV-VIS spectrophotometer at $\lambda_{\text{max}}=599\text{nm}$. All the adsorption experiments were conducted in duplicate, and the mean values were reported.

RESULTS AND DISCUSSION

XRD Analysis

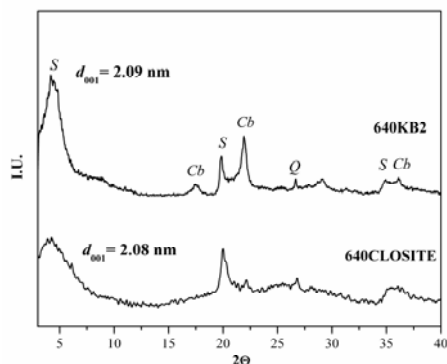


Figure 1. XRD patterns of 640KB2 and 640 CLOISITE; *Cb*–cristobalite, *Q*–quartz, *S*– smectite.

Loading of 640 mg chitosan per 0.5 g for both clays was needed to obtain solely bilayers of chitosan chains confirmed by characteristic d_{001} values (Fig. 1) [1]. The lower loadings lead to formation of monolayers and mixtures of bi- and mono-layers and these samples were not included in further investigation. Besides smectite in both XRD spectra the associated minerals like cristobalite and quartz are also identified.

Adsorption test

The adsorption isotherms of RB5 dye on 640 CLOISITE, 640KB2 and CLOISITE[®] 30B are given in Figure 2.

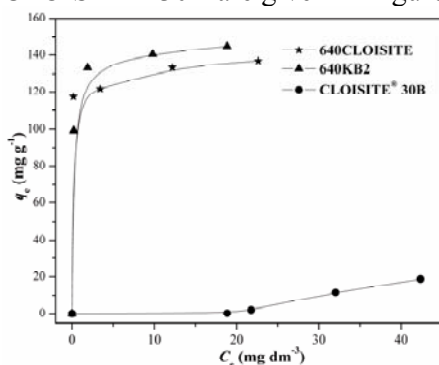


Figure 2. Adsorption isotherms of RB5 removal on 640KB2, 640CLOISITE and CLOISITE[®] 30B.

reported systems [1,4]. These groups can be regarded as active sites that enable interaction with anionic $-\text{SO}_3^-$ groups of RB5 and therefore significantly enhance adsorption capacity.

The adsorption data were fitted with Langmuir and Freundlich models, and corresponding constants were calculated from the intercepts and slopes and given in Table 1.

The adsorption isotherms showed that the 640KB2 and 640CLOISITE have similar uptake of RB5. The adsorption affinity of CLOISITE[®] 30B was significantly lower. The equilibrium amount of adsorbed RB5 on CLOISITE[®] 30B was approx. 30% of the amount adsorbed on chitosan–clay samples. It can be assumed that 640KB2 and 640CLOISITE with intercalated bilayered chitosan chains possessed the additional cationic sites ($-\text{NH}_3^+$), similarly to previously

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 ($\text{dm}^3\text{mg}^{-1}$)	R^2
640CLOISITE	122.2	32.38	0.775	137.93	3.816	0.999
640KB2	117.2	12.20	0.910	166.67	6.000	0.999
CLOISITE® 30B	9.63	2.64	0.916	54.38	0.062	0.993

The correlation coefficient in Langmuir model is closer to unity and therefore this is the most appropriate model for all adsorbents.

CONCLUSION

The promising chitosan-clay nanocomposites with bilayered structure of incorporated chitosan, a green alternative to conventional alkylammonium organoclays, were synthesized using two different clays as starting materials. These eco-friendly nanocomposites had superior adsorption properties in adsorption of the anionic dye Reactive Black 5 in comparison to commercial alkylammonium organo clay (CLOISITE® 30B) having around three times higher adsorption capacity. The chitosan nanocomposites synthesized using the clay from locality Mečji Do (Serbia) showed somewhat better adsorption properties than nanocomposites obtained with commercial CLOISITE® Na⁺.

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REFERENCES

- [1] M. Darder, M. Colilla, E. Ruiz-Hitzky, *Chem. Mater.*, 2003, 15, 3774 – 3780.
- [2] M. Darder, M. López-Blanco, P. Aranda, A. J. Aznar, J. Bravo, E. Ruiz-Hitzky, *Chem. Mater.*, 2006, 18, 1602 – 1610.
- [3] C. M. Futralan, C. C. Kan, M. L. Dalida, K. J. Hsien, C. Pascua, M. W. Wan, *Carbohydr. Polym.*, 2011, 83, 528 – 536.
- [4] M. Darder, P. Aranda, E. Ruiz-Hitzky, "Chitosan-clay bio-nanocomposites" in *Environmental Silicate Nano-Biocomposites*, Eds. L. Avérous and E. Pollet, Springer-Verlag (London), 2012, Ch. 14, pp. 365-391.
- [5] M. Darder, M. Colilla, E. Ruiz-Hitzky, *Appl. Clay Sci.*, 2005, 28, 199 – 208.