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# KINETICS OF ADSORPTION OF MIXED POLLUTANTS BY ORGANOBENTONITE

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#### Abstract

Quantitative substitution of the interlayer cations of smectite by hexadecyl trimethylammonium ions (HDTMA) was performed in order to prepare adsorbent able to simultaneously adsorb toxic metal cations and organic pollutants. The adsorption of Acid Yellow 99 textile dye and Pb<sup>2+</sup> ion from their single solutions and mixture was performed. Kinetics data of adsorption were well represented by pseudo-second-order kinetics model for all investigated adsorption systems.

## Introduction

Simultaneous adsorption of various organic and inorganic pollutants from textile wastewaters by low cost adsorbent is promising technique for their purification [1]. The modification of clay minerals by surfactants is a method to hydrophobize the mineral and therefore to increase the adsorption capacity for organic pollutants. Numerous studies have been focused on the adsorption of nonionic organic compounds onto organo-clay minerals [2-4] and only few on adsorption of metal ions. [5]. The latter revealed that organo-clay minerals have ability to adsorb metal ions. Recently, simultaneous adsorption of various organic and inorganic pollutants has increasingly attracted attention [1]. In this paper local bentonite clay organoclay was used for adsorption of Pb<sup>2+</sup> ion and textile dye Acid Yellow 99 (AY 99) from their single solution and mixture.

# Experimental

Bentonite was obtained from Bogovina, Serbia. It was crushed, ground and sieved through a 74 µm sieve. Hexadecyl trimethylammonium (HDTMA) bromide, Acid Yellow 99 (AY 99) dye and lead (II) nitrate was supplied from Alfa-Aesar Chemical Company, with a chemical purity of 98%, 40% and 99.99% respectively. Na-rich bentonite was prepared by procedure according to [6]. The cation exchange capacity (CEC) of Na-rich bentonite (0.633 mmol/g of clay) was determined by standard ammonium acetate method [7]. The surfactant/bentonite ratio was 0.633

mmol HDTMA-bromide per 1 g of bentonite dried at 110 °C in order to replace all exchangeable cations in interlaminar layer (1CEC value). The solution of HDTMA-bromide was dropedwised added into stirred Na-rich bentonite dispersion. After stirring during 24 h, the dispersion was filtered, washed with distilled water until the filtrate was Br- free (tested with 0.1M AgNO3). The sample was dried at 80 °C [8-9].

All experiments were carried out under conditions: t=25°C, solution volume (v=0.050 dm<sup>3</sup>); concentration of AY 99 or Pb<sup>2+</sup> in single and mixed solution ( $C_0=50$ ) mg dm<sup>-3</sup>); mass of adsorbent ( $m_{adsorb} = 0.01$  g). A period of 24 h was taken as equilibrium although in some experiments equilibrium was reached much earlier. The AY 99 concentration was estimated by Thermo Electron Nicolet Evolution 500 UV-VIS spectro-photometer at  $\lambda_{max}$ =449 nm while the Pb<sup>2+</sup> concentration was estimated by iCAP 6500 Duo ICP, Thermo Scientific Spectrometer at  $\lambda_{Pb}$ =220.4 nm. It was previously confirmed that the presence of Pb2+ in AY 99 solutions did not affect either the position or the intensity of the dye absorption band.

## Results and Discussion

The effect of contact time on the adsorption of AY 99 or Pb2+ from their single and mixed solution onto HDTMA-bentonite is presented in Fig. 1.

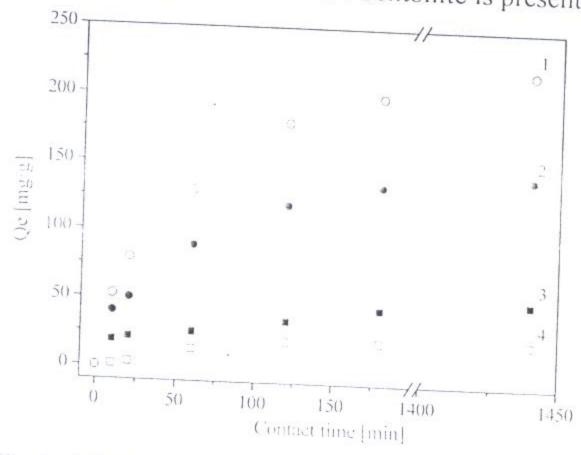


Fig.1. Adsorption of: 1) AY 99 from mixed solution; 2) AY 99 from single solution; 3) Pb<sup>2+</sup> from single solution and 4) Pb2+ from mixed solution

AY99 is better adsorbed from mixture then from single solution, while Pb2+ is better adsorbed from single component solution. The kinetic data were fitted with the pseudofirst-order and pseudosecond-order kinetics models [10]. Since the correlation coefficients for the pseudo-second-order kinetic (r<sub>2</sub>) model were closer to unity, the secondorder kinetics model was considered more adequate.

The pseudo-second-order kinetics model is given in linear form:

$$\frac{I}{q_s} = \frac{1}{k_s q_s^2} + \frac{1}{q_s}$$
(1) where:  $q_s$  is the amount of adsorbed either AY 99 or Pb<sup>2</sup> (mg g<sup>2</sup>) at time  $L_s q_s$ -the amount at equilibrium (mg g<sup>2</sup>). As is the pseudo-second-order rate constant (g mg<sup>2</sup> min ).

The values of  $q_i$ ,  $k_2$  as well as corresponding correlation coefficients (r) are presented in Table 1, together with the experimentally estimated equilibrium amounts  $q_e^{exp}$ .

Table 1. Kinetic parameters for adsorption

Adsorbate	$q_e^{exp}$	9 .	k,	1.
A Y 90	[mg g <sup>-1</sup> ]	[mg g <sup>-1</sup> ]	[g mg <sup>-1</sup> min <sup>-1</sup> ]	
Pb <sup>2</sup>	51.31	166.67	$9.9 \times 10^{-5}$	0.9985
AY99 from mixture	219.25	52.63	$4.8 \times 10^{-4}$	().9995
Pb <sup>2</sup> : from mixture	22.26	250.00	4.7×10 <sup>-5</sup>	0.9985
		23.81	5.6-10	(

The validity of pseudo-second-order kinetic model was confirmed by r coefficient close to unity and good agreement between  $q_{e\,exp}$  and  $q_e$  values.

#### Conclusion

Organobentonite was obtained by modification of local clay (Bogovina) with hexadecyl trimethylammonium ions. The adsorption of Acid Yellow 99 textile dye and Pb2+ ion from their single solutions and mixture was performed. AY99 is better adsorbed from mixture then from single solution, while Pb2+ is better adsorbed from single component solution. Kinetics data of adsorption were well represented by pseudo-second-order kinetics model for all investigated adsorption systems.

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