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Influence of alkali and acidic treatment on sorption properties of Latvian illite clays

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Abstract. The adsorption of monovalent organic cationic methylene blue dye on natural and modified with hydrochloric acid and sodium hydroxide Latvian clay samples from water solutions has been studied. It was established that alkali and acidic treatment of Latvian clay samples changes their sorption characteristics. It was found that increasing concentration of hydrochloric acid from 5 mass % up to 15 mass % decreases adsorption of clay samples proportionally to the acid concentration. Increasing concentration of sodium hydroxide from 5 mass % to 15 mass %, BET specific surface area of the modified clay samples is smaller than BET specific surface area of the natural clay sample. The studies have proven that adsorption ability of Latvian clays is sufficient for using them in waste water purification from admixtures of organic dyes.

Introduction

Latvian illite containing clays, due to their wide distribution, physical-chemical and colloidal properties, have potential application as low-cost and eco-friendly adsorbents for industrial waste purification from organic dyes [1], for discoloration of rapeseed oil [2], petroleum, oil [3] and heavy metals [4]. The increasing interest towards modified clays is explained by necessity to create environmentally safe sorbents. Clays can be modified with inorganic acids and metal salts, which are part of the clay [5], alkali [6], etc. The aim of this work is to study sorption properties of natural and modified Latvian illite clay samples depending on alkali and acidic treatment conditions.

Materials and Methods

Materials. Latvian illite containing clay samples from Tūja (Devonian), Laža (Quaternary) and Strēļi (Jurassic) deposits were studied. Non-modified clay samples were taken from deposits, mechanically cleared from additions, crashed in a pestle, dispersed and swollen in distilled water for 1 month. Swollen clay samples were fractionated by wet sieving through 230 mesh (63 μm) sieve and dried in 105°C temperature. The acidic modified clay samples were prepared from natural clay samples by hydrochloric acid treatment in a glass bulb provided with a cooling pipe on water bath at 95°C for four hours, similar to shown in [7]. The ratio of acid to clay mass was 10:1. After acidic treatment, the samples were washed in distilled water by decantation until pH 3-4 then dried at room temperature. The samples were obtained by using 5, 10 and 15 mass % of hydrochloric acid solutions. The alkali modified clay samples were also prepared from natural clay samples by sodium hydroxide treatment in a glass bulb provided with a cooling pipe on water bath at 80°C for one hour, following the methodology described in the source [8]. Alkali to clay mass ratio was 10:1. After alkali treatment, the samples were washed in distilled water by decantation until pH 7, and then dried at room temperature.

Sample Characterization. Mineralogical composition of obtained clay samples was analyzed by X-ray powder diffraction (XRD) (X'Pert Pro, Philips, The Netherlands). Elemental characterization of the natural and modified clay samples were analyzed by energy-dispersive X-ray spectroscopy

(EDX) (Inca Energy 350, Oxford Instruments). Specific surface area of the samples was measured using the BET method utilizing adsorption of N_2 gas (purity 99.99%) at 77K (Quadrasorb *SI*-KR/MP, Quantachrome Instruments, USA). For this purpose, 0.02 – 0.30 g of the composition samples were outgassed for 4 h at 200°C.

Adsorption of methylene blue. 0,5g dried clay sample was added to 50 ml of aqueous solution of methylene blue with initial concentration 2 g/l and then shaken in Biosan Multi-Shaker PSU 20 shaker type. It was established that the concentration became constant after 24 – 30 hours of shaking. 10 ml of the equilibrated solution was separated from the clay by centrifugation (4 minutes at 6500 rpm). The concentration of methylene blue from water solutions was determined using „Jenway 6405 UV/VIS" spectrophotometer, measuring visible spectra at 582 nm in static conditions at room temperature ($t = 20 \pm 1\ ^0C$). The optical densities were converted to concentrations by reference to calibration data. The adsorption experiments were performed in triplicate.

Results and discussion

Fig. 1. shows the XRD patterns of acidic and alkali modified clay samples from Streļi deposit. During the alkali and acidic action on the sample, an important change in the mineralogical composition occurs. The acid treatment leads to severe mineral crystal structure alteration which is shown characteristic peaks lowering on the patterns, indicating a decrease in the regularity of the mineral structure. As it can be seen, the content of calcite and hematite in the clay samples decreases proportionally with increasing of hydrochloric acid concentration, but quartz content is proportionally increased due to loss of hematite mass. Active amorphous silica gel formation occurs. Mineralogical composition of clay samples modified with sodium hydroxide shows that content of calcite, hematite, quartz and illite in the clay samples decreases when sodium hydroxide concentration increases from 5 to 15 mass %. Similar tendencies were also observed with clay samples from Tūja and Laža deposits.

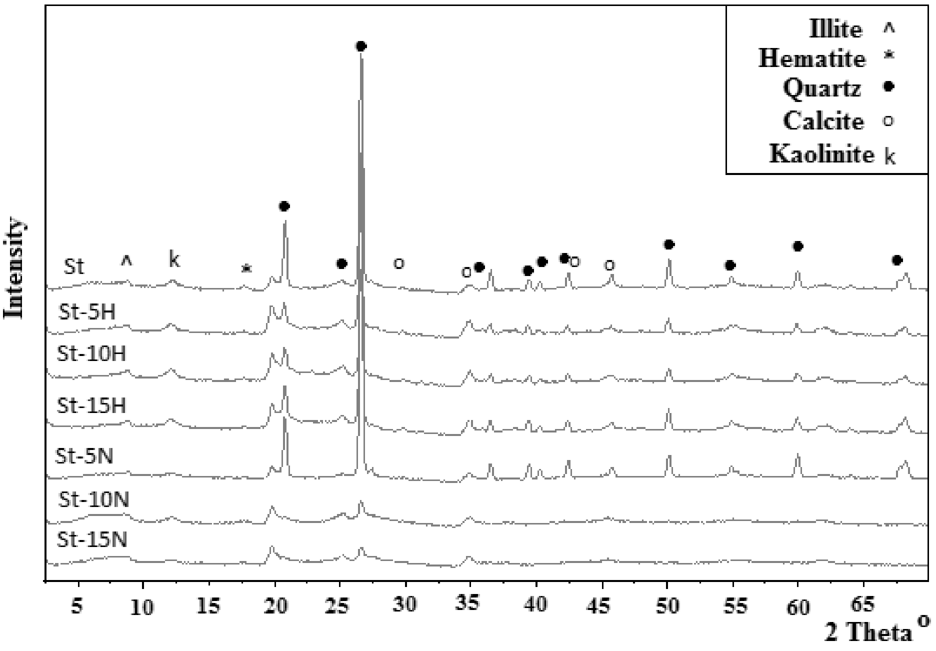

Fig.1 XRD patterns of natural and acidic and alkali modified clay samples from Streļi deposit: St – non modified clay sample; St-5H; St-10H; St-15H – clay samples, treated with 5%, 10% and 15% HCl; St-5N; St-10N; St-15N – clay samples, treated with 5%, 10% and 15% NaOH.

Elemental characterization of the natural and acidic and alkali modified clay samples is shown in table 1. The content of iron, magnesium, calcium, some silica and alumina decreases in the samples treated with 5-15% HCl. Sodium hydroxide removed some silica from the samples, but was less effective in removing the other constituents than HCI.

Table 1 Elemental characterization of the natural and modified clay samples

Sample code	Mean amount of the elements in natural and modified clay samples, [mass %]											
	C	O	Na	Mg	Al	Si	K	Ca	Ti	Fe	Zn	Total
St	6.56	58.76	0.04	1.14	9.17	20.88	1.75	0.00	0.35	1.35	-	100.0
St-5N	9.02	53.76	0.14	1.46	9.70	20.10	1.91	0.61	0.59	2.32	0.39	100.0
St-10N	5.71	59.49	0.46	1.36	9.73	19.66	1.62	0.49	0.30	1.20	-	100.0
St-15N	5.48	56.73	0.66	1.59	10.02	20.63	1.94	0.64	0.47	1.85	-	100.0
St-5H	8.72	57.22	-	0.56	3.38	29.28	0.85	-	-	1.20	-	100.0
St-10H	14.51	56.86	-	0.59	6.28	19.73	0.89	-	0.53	0.62	-	100.0
St-15H	9.57	56.85	-	0.21	2.36	12.87	0.25	-	17.46	0.43	-	100.0

Methylene blue adsorption is largely used nowadays as an accurate and efficient procedure for cation exchange capacity (CEC) determination [9]. Fig.2 shows methylene blue adsorption isotherms on natural and acidic and alkali modified Latvian clay samples from Strēļi deposit.

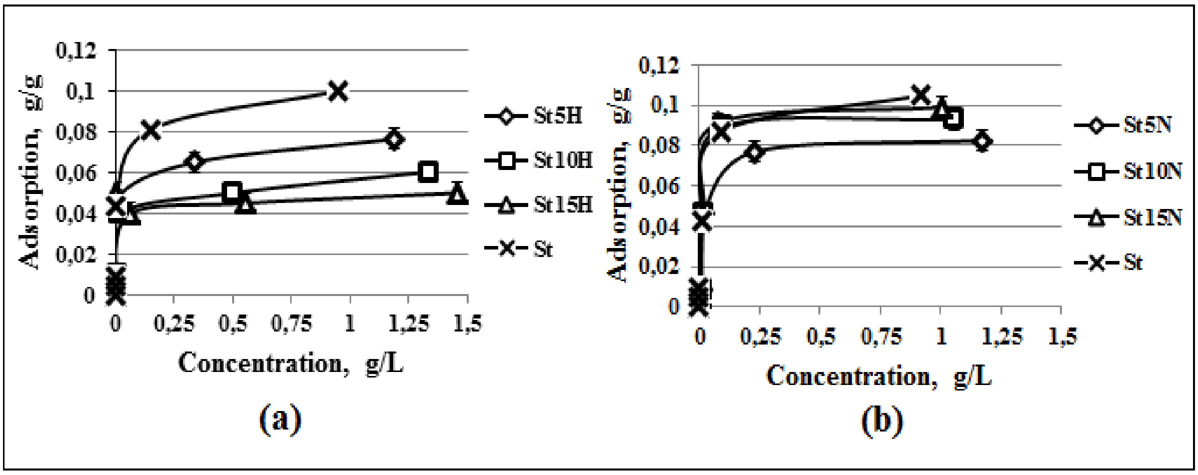

Fig. 2 Methylene blue adsorption isotherms on acidic (a) and alkali (b) modified Latvian clay samples

The isotherms demonstrate influence of the acid and alkali concentration used for modifying. The values of the CEC estimated from methylene blue adsorption isotherms decreases as the acid concentration increases. The decreases in CEC were correlated with the losses of metals from the lattice, again indicating the decomposition of a part of the clay. The values of CEC increases with the increasing of alkali concentration (see Table 2). The acidic treatment affects surface areas more than the alkaline treatment. The increase of the BET surface area under acid treatment may be caused by production of finely dispersed silicon oxides from destruction of mineral structures, removal of amorphous Al or silica components plugging surface pores. A large value for the BET surface area is important for catalytic activity of acidic modified clays.

Under alkaline conditions, similar processes may occur together with accumulation of Fe and Mg compounds (see Table 1). Similar tendencies were also observed with clay samples from Tūja and Laža deposits.

Table 2 BET specific surface area and CEC of natural and modified clay samples

Sample code	Modifier concentration, [mass %]		Treatment conditions		BET specific surface area, [m^2/g]	CEC, [meq/100 g]
	HCl	NaOH	t, [^oC]	[h]		
St	-	-	-	-	32,9	27,9
St-5H	5	-	95	4	54,7	16,5
St-10H	10	-	95	4	92,6	14,1
St-15H	15	-	95	4	100,0	10,7
St-5N	-	5	80	1	18,7	16,5
St-10N	-	10	80	1	26,2	22,9
St-15N	-	15	80	1	29,9	25,4

Summary

For the first time, the influence of the acidic and alkali treatment on the sorption properties of the clay samples from Strēļi, Tūja and Laža deposits were characterized. Modifying with NaOH and HCl solutions changes the adsorption properties of natural clay samples. The acidic treatment affects BET surface area of the investigated samples more than the alkali treatment. The values of the CEC estimated from methylene blue adsorption isotherms decreases as the acid concentration increases. The decreases in CEC were correlated with the losses of metals from the lattice, again indicating the decomposition of a part of the clay.

Acknowledgements

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