



## Phase Composition Studies of the Clays of Urgut District, Uzbekistan and their Application in the Sorption of Some Bivalent Ions

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### ABSTRACT

The work was dedicated to the investigation of phase composition of the sorbents obtained from different clays samples in Urgut district. It was shown that phase composition of the sorbents consists of kaolinite, quartz, corundum, and others. Existence of above mentioned substances in the samples testifies displaying their sorption capacity. Sorption isotherms of some two valent ions by the sorbents have been studied, the coefficients ( $G_{max}$ ,  $K$ ) of Langmuir equation determined and the possibilities for using them as ion-exchanger estimated.

**Key words:** Clay, Sorbent, Diffractogram, Kaolinite, Quartz, Corundum, Sorption isotherm.

### 1. INTRODUCTION

It is known that some clays are used for the preparation of ceramics, various coatings, sorbents, and for another purposes [1]. Expanding the applicability bound of that kind of clays and optimizing the process are determined with the level of investigation of their composition. At the same time, studying a formation mechanism of multiphase system from clay, which is a disperse system allows to obtain polyphase powders from it.

X-ray diffraction (XRD) method that is characterized with its simplicity, high accuracy, and reality of an analysis in solving above mentioned problems provides an effective identification of powders [2].

The resulting diffractogram includes the phase composition of the sample investigated, the crystal structure of phases and characteristics (the sizes of areas of coherent dispersion, microdeformation of cells, etc.) of the microstructures. These characteristics can be determined by Rietveld method [3]. The essence of the Rietveld method is an iterative refinement of the initial approximations of profile and structural parameters in the process of fitting the calculated profile of diffraction to the experimental. In this case, the convergence and accuracy of the method depends on the quality of modeling the lines shape and background components of diffractogram, as well as on the microstructural characteristics of phases. To approximate, the shape of the lines are

most frequently used multivariable distribution of Pearson and pseudo-Voigt and backgrounds - Some polynomials in set form [4]. Bish and Howard [5] have offered a method for quantitative X-ray phase analysis, based on the method of Rietveld and known structures of the phases of sample components that may be determined in the analysis of the diffraction parameters. Using the method [5], a high accuracy determination of the mixtures parameters may be achieved. Therefore, the place of XRD method is incomparable in investigation of phase composition of the sorbents obtained from some clays samples.

#### 1.1. Purpose of the Work

Study the phase composition of the sorbents obtained from clays of some territories in Urgut district by X-ray phase diffractometry and investigating sorption of some ions by them.

### 2. SOURCES AND METHODS OF RESEARCH

The sorbents obtained from clays of different territories in Urgut district were used for investigations. Samples identification has been carried out on the basis of a diffractogram taken on computerized XRD-6100 (X-ray diffractograph, Shimadzu, Japan). To take a diffractogram  $\text{CuK}_\alpha$  - radiation ( $\beta$ -filter, Ni, 1.54178 current regime and tensions given to tube accordingly 30 mA and 30 kV) and the constant speed (correspondence

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to each other  $\omega/2\theta$ ) of  $4^\circ/\text{min}$  rotation with  $0.02^\circ$  step of the detector have been applied, the scanning angle was changed from  $3^\circ$  to  $80^\circ$ . In registering the experiments, a rotating camera was applied and its rotation speed was  $30 \text{ rot}/\text{min}$  (The diffractograms were taken in an instrument, which is for public use at the Institute of Bioorganic Chemistry in Academy of Sciences in the Republic of Uzbekistan). Diffractograms of some samples are presented in Figure 1.

Samples of the special clays that are used for making “tandir” (an oven for baking scones) by local people were brought from Go’s, Sariqtepa and Nisbat villages territories in Urgut district. They were cleaned from various admixtures and plants roots and sieved. To obtain sorbents from clays samples they have been repeatedly washed with distilled water (minimum 10 times) in order to purify them from water soluble salts, separated from a solution by decantation method. The separated samples were calcined in muffle furnace at temperatures of  $800^\circ\text{C}$ ,  $900^\circ\text{C}$ ,  $1000^\circ\text{C}$  (when the samples were calcined in the furnace at the temperature higher than  $1100^\circ\text{C}$  a solid – brick like mass was taken). Obtained sorbents samples were crushed and divided into fractions by sieving. Their phase composition (mainly kaolinite – 89.2%; quartz  $\text{SiO}_2$  – 7.6%; and other admixtures – 3.2%) was determined and their geometric, as well as sorption characteristics were studied.

It is known that the followings are the causes of displaying high absorbing property in clay minerals and they provide possibilities to use clay minerals as ion-exchangers:

- Quantity of increased non-compensated charges equals due to adsorption of the cations in the result of bonds destroy at the edges of aluminum silicon groups

- Exchange of four valent silicon that is on tetrahedral layer in the structure to aluminum and change of three valent aluminum that is on octahedral layer to low valent cations (usually to magnesium) leads to appearance of non-compensated charges in some clay-like minerals structure
- Exchange of hydrogen in external hydroxide group to cation.

Speed of exchange process depends on the nature of clay-like mineral, cations concentrations, as well as on nature and concentration of anions.

### 3. RESULTS AND THEIR DISCUSSION

Considering the samples of the sorbents obtained from clays consist basically of Al, Si, O, H elements and at the first stage, the intensities of X-rays were calculated from diffractograms of the samples [6-10]. The structures and diffractograms of phases, which are in clays composition have been registered in American Mineralogist Crystal Structure Database.

The intensity of the diffracted X-rays was determined with the superposition of waves dispersed by different atoms in one elementar cell [11].

$$I_{hkl}(\theta) = A(\theta) \left| \sum_j f_j(H_{hkl}) \exp(i2\pi(hx_j + ky_j + lz_j)) \right|^2 \quad (1)$$

Where, h, k, and l - the set of integers that define the possible reflection of X-rays for a given crystal lattice;  $A(\theta)$  – a hardware function; j – number of an atom in the elementar cell;  $(x_j, y_j, z_j)$  – relative coordinates of the atoms in the elementar cell;  $f_j(H_{hkl})$  – atomic factor of scattering (form-factor) of the radiation of  $j^{\text{th}}$  atom

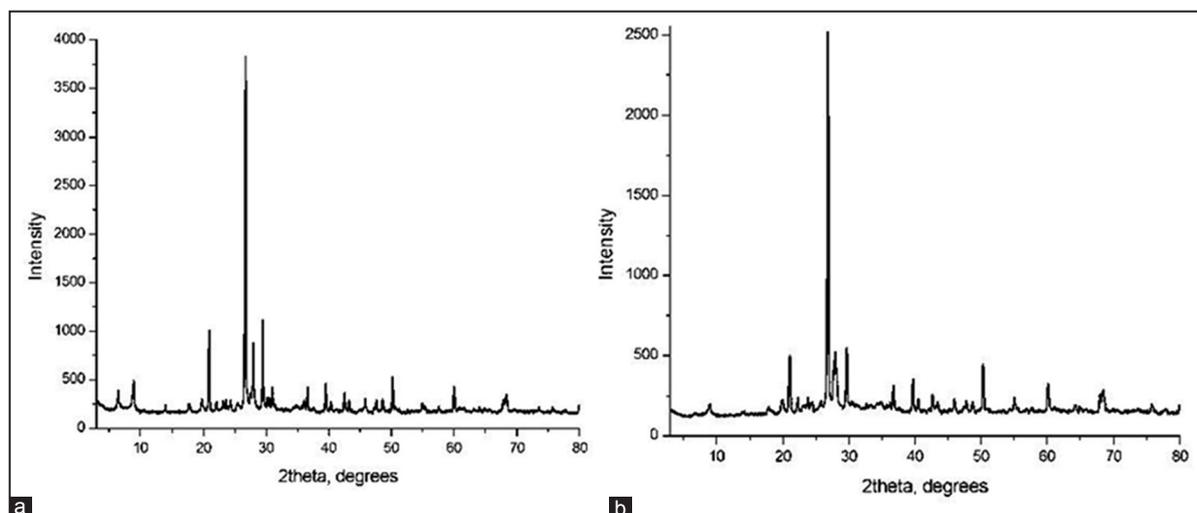


Figure 1: (a and b) Diffractograms of the sorbent samples.

in a direction corresponding to the vector of inverse lattice  $H_{\text{hkl}}$ .

The value of form-factor depends on the number and distribution of electrons of the atom, and the wavelength and the scattering angle of the radiation. Its calculation was done according to Khoperskiy and Yavna [7] on the following formula:

$$f_j(H_{\text{hkl}}) = \int_0^\infty \rho_j(r) \frac{\sin(H_{\text{hkl}}r)}{H_{\text{hkl}}r} r^2 dr \quad (2)$$

Where,  $r$  - radius vector of the point of space;  $\rho_j(r)$  – the electron density of  $j^{\text{th}}$  atom.

Calculation of the peak intensities of the diffracted X-rays carried out with the use of ABINIT software. To describe the profile of the lines was used hardware function - pseudo-Voigt, which is a linear combination of Gaussian and Lorentzian contributions with weights determined by the variable parameter  $\eta$  [11]:

$$A(\theta) = A_0 \left( \begin{array}{c} \eta \frac{2}{\pi H_k} \left[ 1 + 4 \left( \frac{2\theta - 2\theta_0}{H_k} \right)^2 \right]^{-1} + \\ (1 - \eta) \frac{2\sqrt{\ln 2}}{\sqrt{\pi} H_k} \exp \left[ -4 \ln 2 \left( \frac{2\theta - 2\theta_0}{H_k} \right)^2 \right] \end{array} \right) \quad (3)$$

Where,  $A_0$  – peak intensity;  $H_k$  – variable parameter;  $2\theta_0$  – angular position of the center of diffraction line;  $2\theta$  – angle between the incident and diffracted rays.

Analyzing X-rays diffractograms, indexing them and identification of phases structure based on them have been carried out by Powder X [11] and Match! Programs.

The values received on the diffraction maximums angles ( $2\theta$ ) and their intensities (height, in cm), that is to say that the diffraction maximums characteristics are outlined in Table 1. Based on the data presented

**Table 1:** Characteristics of diffraction maximums.

2θ	D <sub>exper.</sub> , Å	l, cm	I/I <sub>0</sub> , %	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
				d <sub>exper.</sub> , Å	d <sub>exper.</sub> , Å	d <sub>exper.</sub> , Å
64,585	136,749	127	5			
88,896	993,953	192	7			
197,386	449,413	88	3	445,831		445,831
209,111	424,472	600	22	436,330		425,565
264,000	337,332	134	5	333,938		333,989
266,916	333,712	2714	100	333,938		334,363
275,000	324,083	95	4			
276,000	322,932	88	3	322,769		
279,636	318,815	468	17	318,971		
294,791	302,760	690	25	306,393		
301,683	295,999	82	3	297,499		297,499
304,841	293,004	83	3	293,578		297,578
309,910	288,326	160	6	290,250		290,250
365,977	245,339	192	7	245,539	255,105	247,500
395,198	227,846	239	9	227,048		228,136
424,957	212,553	166	6	211,343		212,782
432,568	208,988	106	4	208,368	208,368	208,064
458,416	197,788	105	4	196,234	196,234	197,992
476,095	190,847	102	4	190,331		190,331
486,017	187,181	101	4	187,108		187,108
501,898	181,624	316	12	181,740		181,797
600,017	154,056	239	9	153,138	154,507	154,167
67,7945	138,120	108	4	137,236	140,461	138,219
682,000	137,397	134	5	137,236	137,386	137,208
683,200	137,185	120	4	137,236	137,386	137,419
799,200	119,937	83	3	120,175	118,980	119,988

in the Table 1, an approach on the determination of layer minerals structure was thoroughly highlighted in Knyazov and Suleymanov [2]. This approach has been applied for studying phase composition of the sorbents obtained from different clays samples by the method of X-ray phase diffractometry.

It is shown from the data in the Table 1 that the experiment results and intensities of the peaks in diffractograms obtained individually correspond to each other in allowed error limit. With the help of these criteria, the type of the crystal is determined.

Thus, X-ray phase analysis carried out on above mentioned approach gives reliable results in identification of phase composition of the sorbents investigated. Identification results of their structures on an example of kaolinite are presented in Figure 2 and its crystal structure in Figure 3.

On the basis of findings, the phase content of the sorbents obtained from different clays samples gathered from various territories in Urgut district was established. According to them, the main composition of the sorbents consists of kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ;  $a=5.1554 \text{ \AA}$ ,  $b=8.9448 \text{ \AA}$ ,  $c=7.4048 \text{ \AA}$ ,  $\alpha=91.7^\circ$ ,  $\beta=104.862^\circ$ ,  $\gamma=89.822^\circ$ ), quartz ( $\text{SiO}_2$ ;  $a=4.9140 \text{ \AA}$ ,  $b=4.9140 \text{ \AA}$ ,  $c=5.4050 \text{ \AA}$ ,  $\alpha=90.0^\circ$ ,  $\beta=90.0^\circ$ ,  $\gamma=120.0^\circ$ ), corundum ( $\text{Al}_2\text{O}_3$ ;  $a=4.7592 \text{ \AA}$ ,  $b=4.7592 \text{ \AA}$ ,  $c=12.9918 \text{ \AA}$ ,  $\alpha=90.0^\circ$ ,  $\beta=90.0^\circ$ ,  $\gamma=120.0^\circ$ ). Their amounts are, respectively, 89.2%, 7.6%, and 3.2%.

Thus, the phases components of the sorbents obtained from different clays samples are kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), quartz ( $\text{SiO}_2$ ), corundum ( $\text{Al}_2\text{O}_3$ ), and they display high sorption properties and the OH group in kaolinite displays a cation-exchanger property at the expense of hydrogen in them [12]. It is a recommendation for using the clays samples as sorbents.

Sorption of cations on the sorbents obtained from clays samples is determined by drawing a sorption isotherm in variable concentration method in static condition. For this, a series of monocomponent model mixture of the given cations have been prepared. To the sorbent samples with a mass of 5 g by 50 ml model solutions with different concentration were added. When the process ended, the suspension was filtered. Residual concentration of the cations has been determined by the methods of spectrophotometry and ion chromatography. The cations concentrations were determined from the dependence between chromatographic peak and concentration by interpolation method.

On the basis of findings,  $G_{\text{max}}$  and adsorption equilibrium constant  $K$  are determined by solving Langmuir equation on linear graphic method.

$$\frac{1}{G} = \frac{1}{KG_{\text{max}}} + \frac{C}{G_{\text{max}}} \quad (4)$$

Where,  $C$  – solution concentration, mmol/L;  $G$  – adsorbed ion amount, g/L;  $G_{\text{max}}$  – maximum adsorption. As an example a dependence graph of  $C/G$  on  $C_{\text{Ca}^{2+}}$  is presented in Figures 4 and 5. It is shown from that value of  $1/G_{\text{max}}$  is 0.5668, from that  $G_{\text{max}}=1.7643 \cdot 10^{-4}$  mmol/L and  $K=1.15 \cdot 10^3$ .

Thus sorption isotherms of  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$  ions by investigated sorbents samples have been studied and  $G_{\text{max}}$  and  $K$  values for them are presented in Table 2 on the example of the sorbent obtained from clay of Nisbat village in Urgut district at temperature of  $80^\circ\text{C}$ .

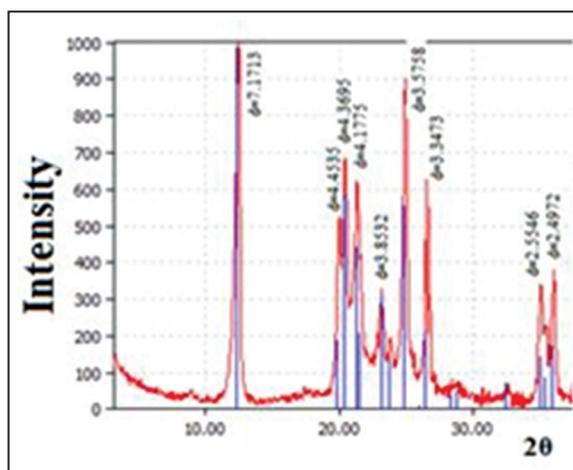


Figure 2: Identification results of the structure of kaolinite determined from composition of the sorbent sample obtained from clay.

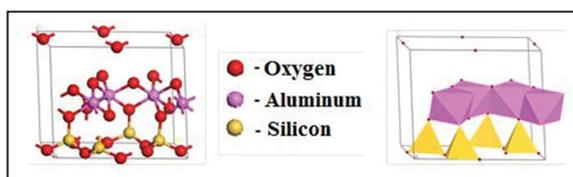


Figure 3: Crystal structure of kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_9\text{H}_4$ ).

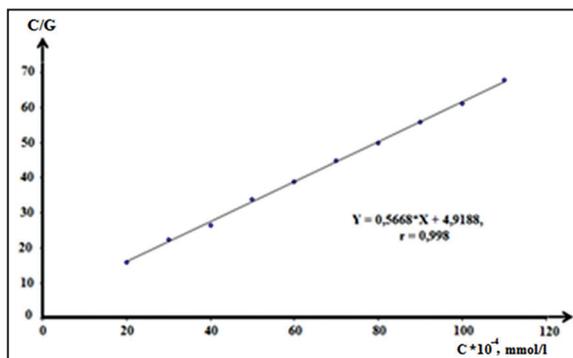
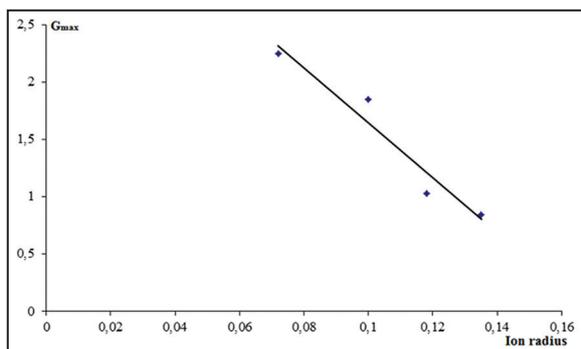


Figure 4: The dependence of  $C/G$  on  $C$ .



**Figure 5:** The dependence of maximum adsorption values  $G_{\max}$  of ions on their ion radius on given sorbents.

**Table 2:**  $G_{\max}$  and  $K$  values, which describes sorption of different ions by the sorbents obtained from clay of Nisbat village in Urgut district at temperature of 800°C.

Ion	$G_{\max}$ , mmol L <sup>-1</sup>	$K$	$r^2$
Mg <sup>2+</sup>	$2.25 \times 10^{-4}$	$2.76 \times 10^3$	0.998
Ca <sup>2+</sup>	$1.76 \times 10^{-4}$	$1.15 \times 10^3$	0.998
Sr <sup>2+</sup>	$1.03 \times 10^{-4}$	$3.72 \times 10^3$	0.980
Ba <sup>2+</sup>	$0.84 \times 10^{-4}$	$6.32 \times 10^3$	0.978
Cr <sup>3+</sup>	$1.21 \times 10^{-4}$	$1.52 \times 10^3$	0.964
Cu <sup>2+</sup>	$0.78 \times 10^{-4}$	$8.21 \times 10^3$	0.966
Fe <sup>3+</sup>	$0.67 \times 10^{-4}$	$4.65 \times 10^3$	0.958
Pb <sup>2+</sup>	$0.47 \times 10^{-4}$	$3.18 \times 10^3$	0.962

It is shown from the data outlined in the table that two and three valent ions are retained on the sorbent investigated on ion exchange mechanism. At the same time,  $G_{\max}$  value depends on the radius of the ion adsorbed. This dependence is quantitatively estimated through the dependence of ion radii of the main group elements in II group on their maximum sorption ( $G_{\max}$ ) values on a given sorbent. According to Figure 5, the studied dependence level is relatively high (correlation coefficient value makes 0.969) and an increase of ion radius leads to linear decrease of sorption.

On the whole, it can be concluded that the sorbent can be used for the sorption of studied ions from their solutions.

#### 4. CONCLUSIONS

1. The phase composition of the sorbents obtained from different clays samples in Urgut district was investigated by X-ray phase diffractometry, it was shown that their phase compositions consist of kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), quartz ( $\text{SiO}_2$ ), corundum ( $\text{Al}_2\text{O}_3$ ), and others
2. The sorbents displaying high sorption properties because they have kaolinite, quartz, corundum in their composition, the OH groups in kaolinite displaying cation-exchanger property because of

hydrogen is a recommendation for using them as sorbents

3. Sorption isotherms of some ions from solutions on ion exchange mechanism on the sorbents obtained from clays of different territories in Urgut district were studied
4. Linear dependence of adsorption on inverse values of the ion radius was quantitatively estimated.

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#### 5. REFERENCES

1. Y. S. Karabasov, (2002) *New Materials, Under Science Issue*, Moscow: MISiS, p475-488. (In Russian).
2. A. V. Knyazov, E. V. Suleymanov, (2005) Fundamentals of X-ray phase analysis, *Educational-methodical Textbook*, p3-23. (In Russian).
3. A. S. Kasprzhitskiy, G. I. Lazorenko, A. V. Morozov, V. A. Yavna, (1993) The Rietveld method. In: R. A. Young, (Ed.), *IUCr Monographs on Crystallography*, Vol. 5. Oxford: Oxford University Press. p132-166.
4. G. Will, (2006) *Powder Diffraction: The Rietveld Method and the Two Stage Method to Determine and Refine Crystal Structures from Powder Diffraction Data*, Berlin Heidelberg: Springer Science & Business Media. p134-194.
5. D. L. Bish, S. A. Howard, (1988) Quantitative phase analysis using the Rietveld method, *Journal of Applied Crystallography*, **2**: 86-91.
6. A. Altomare, M. C. Burla, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Rizzi, (2001) Quanto: A Rietveld program for quantitative phase analysis of polycrystalline mixtures, *Journal of Applied Crystallography*, **34(3)**: 392-397.
7. A. N. Khoperskiy, V. A. Yavna, (2004) Radiation of photon by multielectron system, *Energiya*, **276**: 4-10. (In Russian).
8. D. L. Bish, R. B. Von Dreele, (1989) Rietveld refinement of non-hydrogen atomic positions in kaolinite, *Clays and Clay Minerals*, **4**: 289-296.
9. D. L. Bish, (1993) Rietveld refinement of the kaolinite structure at 1.5 K, *Clays and Clay Minerals*, **6**: 738-744.
10. C. Dong, (1999) Powder X: Windows-95-based program for powder X-ray diffraction data processing, *Journal of Applied Crystallography*, **32**: 838-838.
11. A. S. Kasprzhitskiy, G. I. Lazorenko, A. V. Morozov, V. A. Yavna, (2012) Identification of structure features of layer minerals by the method of X-ray diffraction, *Don Engineer Bulletin*, **23**: 4-2.
12. N. Q. Muhamadiev, S. M. Sayitkulov, K. M. Saidov, (2015) Sorption of two valent ions on the sorbents obtained from some clays, *Samarkand State University Bulletin*, **3**: 125-128. (In Uzbek).

**\*Bibliographical Sketch**



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