

## SORPTION OF $\text{Cu}^{2+}$ IONS ONTO DIATOMITE CONSTITUENTS

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**Abstract:** Studies of the sorption capacity towards  $\text{Cu}^{2+}$  ions of diatomite from the Ghidirim location of RM, as well as of the extracted clay phase are presented. Separated clay fraction from diatomic material is clean enough, and especially is rich in montmorillonite. Maximum sorption capacity for studied clay fraction is achieved by rising the temperature of calcination treatment up to 200°C. At higher temperatures the lattice of montmorillonite is contracted and its sorption capacity towards  $\text{Cu}^{2+}$  ions decreases strongly.

**Keywords:** diatomite, sorption of  $\text{Cu}^{2+}$  ions.

### Introduction

Elimination of heavy metals from water is an important public health issue. Proposed methods for the removal of heavy metals include chemical precipitation, membrane filtration, ion exchange, alum coagulation, and adsorption. Adsorption is considered a reliable process that can be used to remedy a mixture of contaminants with low concentration. An efficient material that can be used, especially at a low cost, is diatomite or diatomaceous earth. Its physical and chemical properties such as high porosity, high permeability, small particle size, and large surface area, makes diatomite suitable for a wide range of industrial applications. Recently, many attempts have been made to increase sorption capacity of natural adsorbents toward heavy metals by chemical modification of their surface [1-5]. Despite the efforts made to utilize diatomite as an adsorbent, more studies on increasing its adsorption capacity are needed. In the Republic of Moldova significant deposits of diatomaceous earth are localized along course of the Dniester, on the sector Naslavcea – Camenca. Recently studies demonstrated that the mineral phase of the diatomite from the Ghidirim location contains a number of clay minerals, like montmorillonite (in a mixture with insignificant quantities of slightly chloritized montmorillonite), illite and kaolinite [6]. The diatomite contains also non-clay components as fine dispersed quartz and amorphous material, the more probable sources of which are opal, amorphous aluminosilicates, aluminum and iron hydroxides. For extension of the field of application of diatomites, as well as intensification of their usage efficiency, the common procedures are the modification of the surface chemistry or the concentration of the diatomic phase by the elimination of impurities existing in the diatomic raw material. More often, the question is mooted to cleanse the diatomic phase of all other phases, including clay minerals [3-5]. In fact, the clay minerals which are present in the diatomic formations may be of a special interest for certain usage. Consequently, when the question is mooted to cleanse the diatomic formations, the formulation should also include the proceeding of reutilization of the clay components.

Current work includes studies of the separated clay fraction from the Ghidirim diatomite with the purpose to be utilized as mineral adsorbent for the removal of heavy metals from water.

### Experimental

The diatomite from the Ghidirim location of RM was used for investigations. X-ray analysis was performed using the DRON-1 X-ray installation with  $\text{CoK}\alpha$  radiation. Isotherm experiments were conducted by adding 0,5 g of adsorbent into a varied concentration of solution  $\text{CuSO}_4$  in a cleaned stoppered glass bottle, and shaking in an isothermal shaker at 22°C for 24 h. The volume of adsorbate solutions was fixed at 50 mL. After equilibrium time, residual  $\text{Cu}^{2+}$  ions were analyzed by using atomic absorption spectrophotometer.

### Results and discussions

#### *Extraction of the clay fraction from the diatomite*

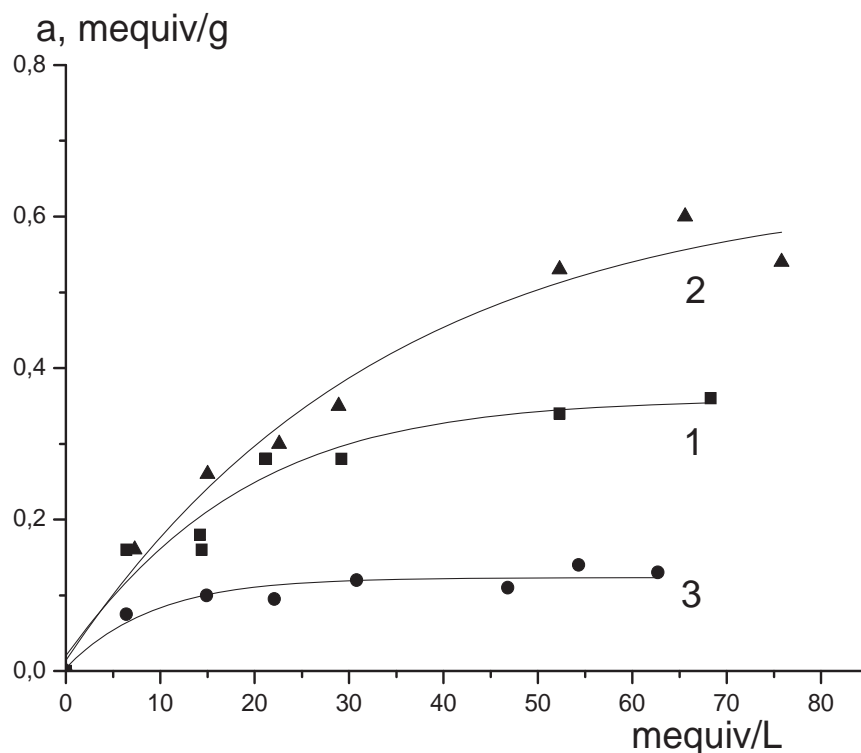
Extraction of the clay minerals from the studied diatomite was performed using the method of sizing by settling in liquid media (distilled water) [7]. The procedure insures “mild” conditions for the extraction of clay constituents without their denaturing or destroying. For the extraction of different constituents from solid materials (soils, sediments, clay formations) are applied various chemical reagents (acids, bases, complexons etc.), however the degree of selectivity and effects on other components should be well-argued by individual investigations of each type of solid material [7]. Aqueous extraction applied in these studies are more easily to perform and, though sizing by settling in liquid media does not insure a complete extraction of all clay constituents from diatomite, such procedure, what is more importantly, does not alter natural chemical composition of clays.

X-ray analysis of the clay fraction extracted from the diatomite shows “clean” and distinctly reflexions (peaks) of the clay minerals and their veraciously behavior on thermal treatment [6]. The presence of montmorillonite, illite

and kaolinit in separated clay fraction is uniquely demonstrated. The initial diatomic material contains some non-clay components, as fine dispersed quartz and amorphous material, the more probable sources of which are opal, amorphous aluminosilicates, aluminum and iron hydroxides. Though some quantities of fine-dispersed quartz also penetrate into the separated clay fraction, these quantities are matchless smaller compared to those which are contained in the initial diatomic material. It is very importantly that the separated clay fraction does not contain amorphous material extracted from the initial diatomic material.

Thus, the applied procedure of clay fraction separation by sizing settling in liquid media proves to be very useful enabling possibilities for more accurate identification of the clay constituents of diatomic material. Also, along with an accurate diagnostics of the clay minerals, it is very important that the applied procedure allows to separate very clean clay fraction especially rich in montmorillonite, which can be utilized itself as mineral adsorbent for practical purposes.

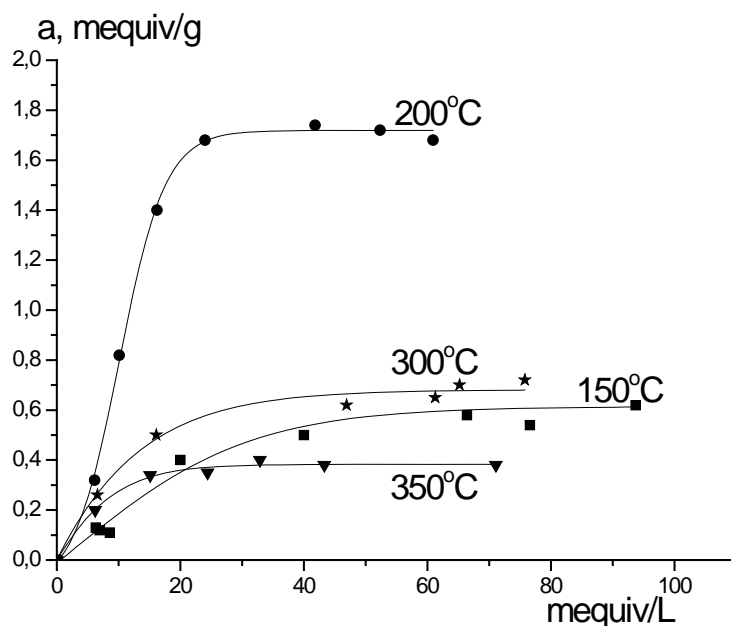
#### Sorption of $\text{Cu}^{2+}$ ions from water solution



**Fig. 1. Sorption isotherms of  $\text{Cu}^{2+}$  ions onto initial (integral) diatomic material (1), onto separated clay fraction (2), and onto non-clay fraction remained after separation of clays from diatomic material (3). Samples dried at  $105^{\circ}\text{C}$ .**

Initial (integral) diatomic material, separated clay fraction and non-clay fraction remained after separation of clays from diatomic material were tested as adsorbents for  $\text{Cu}^{2+}$  removal from water solution. Figure 1 presents sorption isotherms onto these samples dried beforehand at  $105^{\circ}\text{C}$ .

Sorption capacity for initial (integral) diatomic material reaches 0,35 miliequivalents of  $\text{Cu}^{2+}$  ions per gram of adsorbent (or  $\sim 11,2$  mg  $\text{Cu}^{2+}/\text{g}$ ). Sorption capacity for extracted clay fraction from diatomic material reaches 0,57 miliequivalents of  $\text{Cu}^{2+}$  ions per gram of adsorbent (or  $\sim 18,2$  mg  $\text{Cu}^{2+}/\text{g}$ ). Thus, the sorption capacity of the extracted clay fraction is higher than that of initial (integral) diatomic material by about 1,6 times. Sorption capacity of non-clay fraction is lesser, and reaches only 0,12 miliequivalents of  $\text{Cu}^{2+}$  ions per gram of adsorbent ( $\sim 3,8$  mg  $\text{Cu}^{2+}/\text{g}$ ), i.e. less than by about 3 and 5 times, as compared to that for integral diatomic material or extracted clay fraction. To be mentioned, that separated clay fraction from diatomic material is clean enough, and especially is rich in montmorillonite. This mineral possesses more higher sorption properties towards heavy metals than other clay minerals [1]. Non-clay fraction (remained after separation of clays from studied diatomite) is composed of fine dispersed quartz and amorphous material, the more probable sources of which are opal, amorphous aluminosilicates, aluminum and iron hydroxides [6]. In this case, initial (integral) diatomite represents properly summary structure of the diatomic material including clay fraction on the background of the diatomic formation (non-clay components).



**Fig. 2. Sorption isotherms of  $\text{Cu}^{2+}$  ions onto separated clay fraction. Samples calcined at 150, 200, 300 and 350°C.**

Fig. 2 presents sorption isotherms of  $\text{Cu}^{2+}$  ions onto separated clay fraction calcinated beforehand at different temperatures. Calcination treatment at 200°C increases sorption capacity of clay fraction by about 3 times as compared to that for sample dried at 105°C, and reaches ~1,8 miliequivalents of  $\text{Cu}^{2+}$  ions per gram of adsorbent (~58 mg  $\text{Cu}^{2+}/\text{g}$ ). After calcination treatment at 300°C, sorption capacity of clay fraction decreases to ~0,7 miliequivalents of  $\text{Cu}^{2+}$  ions per gram of adsorbent (~22 mg  $\text{Cu}^{2+}/\text{g}$ ), nevertheless this value exceeds by about 2 times sorption capacity of initial (integral) diatomic material.

Spectral analysis used to investigate the hydroxyl species and acid sites on diatomite surface shows the presence of the Lewis and Brønsted acid sites, and various hydroxyl species, including isolated hydroxyl groups, H-bonded hydroxyl groups and physically adsorbed water [2]. The Lewis acid sites in diatomite samples are considered to be resulted from the clay impurities, and the Brønsted acid sites are considered to be resulted from surface silanol groups ( $\equiv\text{Si-OH}$ ) of diatomaceous silica associated with the physically adsorbed water by hydrogen bond. In fact, silanol groups are present also on the edges of the tetrahedral layers of clay minerals, being for montmorillonite an important source of the surface charge and Brønsted acid sites [8]. Delimitation of the Lewis and Brønsted acid sites in diatomite samples as is considered by [2] seems to be equivocal, and to conclude about the role of the surface chemistry of such complex materials as diatomaceous formations it is necessarily to separate adequately its constituents.

To be mentioned, that itself sorption process onto clay minerals is too complex, and can occur in the several forms, selective (specific or non-exchangeable sorption) and non-selective (exchangeable) sorption [1, 8]. In the case of non-selective sorption, clay minerals adsorb ions through exchangeable cations, also certain quantities of ions are electrostatically bound to the surface as counter ions in the diffusion layer which is formed because of the surface charge. Selectively adsorbed ions form inner-sphere complexes with surface hydroxide sites and are primarily bound to the surface of clay minerals by chemical bond. Such bond depends upon the structure of the surface chemistry and exhibits different behavior from electrostatic bonding.

As was mentioned, separated clay fraction from diatomic material studied in this work is clean enough, and especially is rich in montmorillonite. Therefore, it is reasonably to consider that registered dynamics of sorption capacity towards  $\text{Cu}^{2+}$  ions reflects properly dynamics of modification of the surface structure of montmorillonite during calcination treatment.

At moderate temperatures (e.g. up to 105°C, at which in this work clay fraction was dried beforehand), sorption process onto montmorillonite can occur both as selective (specific) sorption and non-selective (exchangeable) sorption. Specific to clay minerals is the presence of isomorphous substitutions in their lattice, e.g. in montmorillonite  $\text{Al}^{3+}$  may be substituted for  $\text{Mg}^{2+}$  in the octahedral layer. This gives rise to an unbalanced negative charge which is compensated for by adsorption on the surface of cations. These cations are exchangeable and are coordinated to water. The water molecules

exhibit the peculiar property of being strongly dissociated, at least when the amount of adsorbed water is at the double layer level or less [9-11]. The enhanced dissociation is ascribed to the polarization effect of the cations to which they are coordinated. In consequence, the surface concentration of mobile protons is increased which is responsible for the Brønsted acidity:



This type of acidity is considered dominating and the acid strength increases on dehydrating. Maximum sorption capacity for studied clay fraction in this work is achieved by rising the temperature of calcination treatment up to 200°C. At higher temperatures the lattice of montmorillonite is contracted as evidenced from X-ray analysis [6], and its sorption capacity towards  $\text{Cu}^{2+}$  ions decreases strongly.

### Conclusions

Studies of the sorption capacity towards  $\text{Cu}^{2+}$  ions of diatomite from the Ghidirim location of RM, as well as of the extracted clay phase are presented. Separated clay fraction from diatomic material is clean enough, and especially is rich in montmorillonite. Maximum sorption capacity for studied clay fraction is achieved by rising the temperature of calcination treatment up to 200°C. At higher temperatures the lattice of montmorillonite is contracted and its sorption capacity towards  $\text{Cu}^{2+}$  ions decreases strongly.

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