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Exploiting the natural potential of romanian kaolin clay. Adsorption capacity improvement through heat treatment

Ş. COJOCARU[a], A. M. DUMITRESCU[b], I. G. BREABĂN[a], A-A. DOMOCOS[c], A. R. IORDAN[b,*],
N. MELNICIUC-PUICĂ[d], M. N. PALAMARU[b]
[a]*Faculty of Geography and Geology, Alexandru Ioan Cuza University of Iaşi, 11, Carol I Blvd., 700506, Iaşi, Romania*
[b]*Faculty of Chemistry, Alexandru Ioan Cuza University of Iaşi, 11, Carol I Blvd., 700506, Iaşi, Romania*
[c]*Faculty of Physics , Alexandru Ioan Cuza University of Iaşi, 11, Carol I Blvd., 700506, Iaşi, Romania*
[d]*Faculty of Orthodox Theology, Alexandru Ioan Cuza University of Iaşi, 9 Closca, 700065, Iaşi, Romania*

Clays are very promising materials to be used in the domain of environmental remediation due to their good adsorption properties of both organic and inorganic ions. The present study analyzes the possible enhancements of a Romanian kaolin type clay's capacity to adsorb organic molecules. The acquired material was calcinated at 350°C and 500°C and then characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The tests were carried out on a methylene blue aqueous solution and UV-Visible spectroscopy was used to determine the dye concentration of the solution before and after conducting the experiments.

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1. Introduction

Clays are phyllosilicates, constituents of soil that have a large abundance in nature, whose composition is mostly made out of clay minerals but which can also contain other minerals like quartz, silica, feldspar, carbonate, volcanic ash or metal oxides [1],[2]. The use of these materials has known a large increase in recent years, their domains of application having greatly diversified from the traditional ones, like ceramics, building materials or pharmaceutical applications to newer ones such as pollutant control, catalysis or the controlled-release of various substances [3],[4]. The easy acquisition of most clay materials, their interesting physicochemical characteristics and their ability to be used without further, expensive, purification makes them a lower costing alternative to other materials, especially in the field of environmental remediation where they can be used as efficient adsorbents, nanofillers for polymers or supports for other nano-catalysts [5].

A great threat to the environment is water pollution by organic substances, which has become a problem increasingly difficult to contain and reduce. Among the polluting substances, dye contamination is one of the most common forms, given the numerous sources of pollution, such as textile, wood, paper, leather, plastic, cosmetic or food industries. The colorants are hazardous to the environment, causing problems by changing the transparency of waters, their chemical compositions, and even by damaging the health of animals and humans alike. Their removal from the environment can be achieved through various biological and chemical methods like coagulation, electro-chemical treatment, oxidation or adsorption [6],[7]. The latter is considered to be a very promising technique, due to the fact that it is easy to apply and non-toxic, the only downside being the use of adsorbent materials that are expensive. Clays are a viable alternative to solve this problem because of their interesting properties, which are a result of their small particle dimensions, constituting elements and internal crystalline structure, that is organized most commonly into alumino-silicate layers [2]. The particularities of each arrangement of layers as well as the main constituting elements of the material divide clays into different types, such as bentonite, montmorillonite, smectite, vermiculite, kaolinite etc. In aqueous solution, clays swell by expanding their interlayer spacings and can attract and exchange different ions. Although they have the ability to remove anions from the solution, most clays present a natural negative electrical charge at their surface, which leads to good cation attraction or exchange properties and, so, a preference for organic compounds. Kaolin is a type of clay which contains kaolinite, having the empirical chemical formula $Al_2Si_2O_5(OH)_4$ and a pure composition of 46,54% SiO_2, 39,5% Al_2O_3 and 13,96% H_2O, but which can also contain fragments of quartz, silica, mica or feldspar. Its internal structure is of type 1:1, which means each particle is formed by two sheets, a tetrahedral silicate layer and a metal oxide or metal hydroxide octahedral layer of which the metal is most commonly Al [8],[9]. The natural electrical charge of this material is slightly negative, giving it the ability to conduct cationic exchanges. In order to ensure good adsorption capacities, certain changes can be made to clays to enhance their natural capabilities. The most common ones are acid activation, surfactant impregnation, intercalation and pillarization but heat treatment can also be employed [10]. Thermal annealing can affect both the physical and chemical properties of the material, such as the swelling degree, particle size, pore structure and cation exchange capability, thus modifying their catalytic and adsorptive capacities [11].

The present study aims to identify possible ways of advancing the use of local Romanian clay deposits in new sectors of science and industry, such as adsorbents of organic water contaminants. Enhancements of the clays' adsorption capacities, which can be achieved by heat treatment, were investigated. The intent is not only to obtain a desirable adsorbent, but also a sustainable one. The material chosen was a locally sourced kaolin clay from Pădurea Craiului area in Romania. The negative impact on the environment was, thus, minimized by reducing the travel costs and the resources used to procure the clay, as well as by stimulating local economy. The tested samples were clays subjected to calcination at 350°C and 500°C and then used in the removal of methylene blue form an aqueous solution. This particular cationic dye was chosen because it has been used in the past as a model pollutant, to assess the adsorption ability of various materials.

2. Experimental

Methods and techniques

The tested clay was in powder form, commercially acquired and used as adsorbent without further chemical purification. The deposit from which the material was originally procured is located in Pădurea Craiului mountains, an area rich in clays that have formed on silicious rocks. Thermal annealing of the sample was conducted at 350°C and 500°C respectively, with the heating technique slightly different for each calcination phase. In the case of 350°C annealing, a Prazitherm electrical sand bath with variable temperature control and a thermostat controller was used, and the temperature of the sample was raised starting from 25°C to 350°C at a rate of 50°C per hour, where it was kept for one hour. In the case of the 500°C heat treatment, it was carried out in a Nabertherm B150 furnace with programmable temperature control. The clay reached the maximum desired temperature in an hour, starting from room temperature value, where it stayed for a period of 5h. Both samples were left to gradually cool down. The three clay specimens tested were labeled K., K.350 and K.500 respectively and characterized using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

In the case of the IR analysis the spectrum was acquired in the 4000-370 cm^{-1} domain using a Bruker Vertex 70 adsorption spectrophotometer. The X-ray diffractograms were obtained using a Shimadzu LabX 6000 diffractometer equipped with a graphite monochromator with Cu Kα radiation that operates at $\lambda = 0.15405$ Å. The scanning was done at room temperature (25°C) from 2° to 80° 2θ angle at a scanning step of 0,02°/s.

The adsorption studies were carried out on an aqueous solution of methylene blue ($C_{16}H_{18}N_3SCl$) (MB) acquired from Merck, with the concentration of 250 mg/L. Two adsorption protocols were followed, in which the total contact time between clay and MB solution differed. Protocol (A) consisted in a quantity of 60 mg of sample added to 30 mL MB stock solution in a Berzelius glass. The mixture was stirred magnetically at 330 rpm for a period of 2h, after which the mixing was stopped and left for 2 more hours as is. In Protocol (B), the same amount of clay and MB was used but the stirring time was increased to 5h, followed by 2h of the mixture left to sit. The total contact time between adsorbent and adsorbate was thus increased from 4 to 7 hours. In both cases, the experiments were conducted at room temperature and in a dark chamber, to prevent potential dye degradation under the influence of visible light. The mixture was filtered to remove the absorbent particles before analysis, after which the equilibrium concentration of the samples were investigated using a UV-Visible Shimadzu 1601 spectrophotometer. The spectrum was acquired in the 200-800 nm wavelength and the MB adsorption maximum peaks were measured at 665 nm. The percentage of dye that was removed from the solution was calculated using the following equation:

$$\text{Dye removal percentage} = \frac{C_i - C_e}{C_i} \times 100$$

where C_i represents the initial concentration of the solution and C_e is the equilibrium concentration of the analyzed solution.

3. Results and discussion

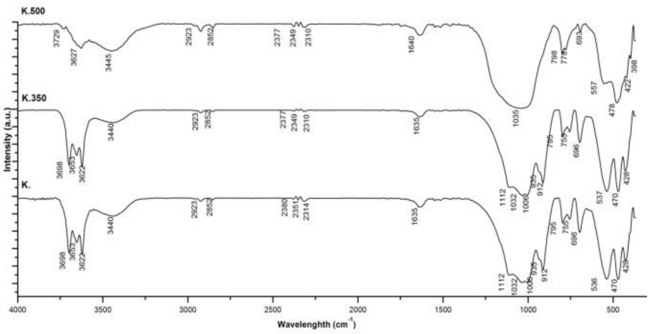

Fig. 1. IR spectrum of the clay samples.

IR Characterization. In clay minerals, infrared spectroscopy is used to analyze their structure in order to identify the placement and intensity of O-H bending absorption bands, as well as the absorption bands characteristic to Si-O and Al-OH bonds. The IR spectrum of the samples (Fig. 1) shows the characteristic absorption bands of kaolinite. A strong band appears at 3697 cm^{-1}, belonging to the in-phase symmetric stretching vibration of the OH bonds, as well as two other, weaker, ones at 3669 and 3653 cm^{-1} which are caused by the out-of-plane stretching vibrations. The inner layer and surface OH groups can be seen in the 950–800 cm^{-1} wavelenghth, in our case they are visible at 912 and 935 cm^{-1} [12],[13]. Adsorbed water generates a wide band that can be observed at around 3440 cm^{-1} and also at around 1635 cm^{-1} [14]. The maximums that appear at 2852 and 2923 cm^{-1} can be attributed to C-H bonds stretching vibration [15]. In kaolinite clay Si-O deformation bonds are visible in general at 1120 - 1000 cm^{-1}, in our case they appear at around 1006, 1032 and 1112 cm^{-1} wavelenghth. Si-O stretching bonds on the other hand can be seen at 696, 755 and 795 cm^{-1} respectively [13],[8]. Si-O-Si and Al-O-Si deformation bonds are visible at 470 and 536 cm^{-1} respectively [8]. Comparing the spectra of the untreated clay sample with the clays calcinated at 350°C and 500°C, certain changes can be seen. The removal of water that comes with increasing the temperature is evident by the decreasing in the intensity of OH bonds found in the 3620 – 3700 cm^{-1} wavelength region. The three Si-O deformation peaks visible between 1120 and 100 cm^{-1} turn, in the case of K.500, into a single band visible at 1035 cm^{-1}, which according to [16] Cristóbal et. al (2010) is a sign of the silica changing from crystalline to amorphous state. Another sign that the structure of the sample tends to become disordered with thermal treatment is the loss of intensity of the Si-O and Al-O-Si band at 696 and 536 cm^{-1} respectively [12],[16],[17]. Noted is the fact that, because kaolin often contains other minerals as well, certain interferences of bands in the IR spectrum are possible. To correctly confirm the structure and composition of the clays tested in this study, X-ray diffraction analysis was employed.

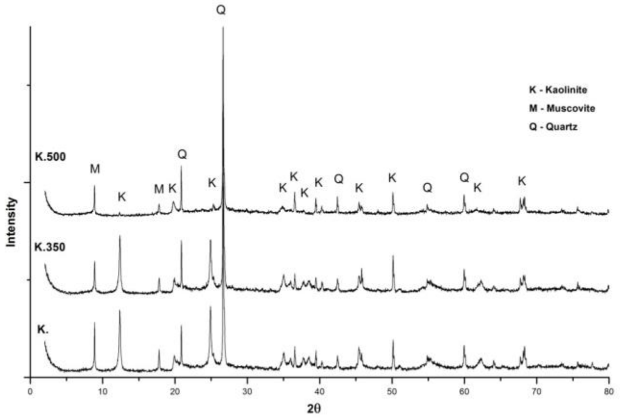

Fig. 2. XRD pattern of analyzed kaolin clays

XRD Characterization. The diffractiograms of the three samples, with the maximum diffraction peaks identified, are presented in Fig. 2. The presence of kaolinite is confirmed by the well defined, characteristic, peaks that appear at the values 12,37°, 20,8° and 24,9° of the 2θ degree [18],[19]. Other species also identified were muscovite and quartz, the latter being represented by the strong peaks found at 20,7°, 26,6° and 59,9° (2θ). The loss of intensity of kaolinite peaks that occurs with the increase in temperature, which also leads to the loss of water, is a sign of the structure of the sample transforming into amorphous state [20],[21]. A change that occurs in the case of the kaolinite peak found at 12,37° (2θ) is the changement in the basal spacing, a measurement that reflects the thickness of aluminosilicate layer, from 7,149 Å for K. to 7,142 Å in K.350 sample and 7,162 Å for K.500, reflecting a certain distortion that develops in the crystallinity of the clay [22],[23]. Evident is also the reduction of the primary kaolinite characteristic diffraction peaks, witout the loss in intensity of the ones attributed to quartz [18]. This is an expected result because, with the increase in temperature, dehydroxylation of kaolin occurs [9]. The loss of OH groups takes place simultaneously with the apppearance of distortions in the materials' structure. Between crystalline and amorphous, a transitional semi-amorphous layer structure appears in the case of kaolin, which is recognized as being metakaolin. This new form of the material is known to develop when the clay is calcinated at about 500 – 550°C [24],[25].

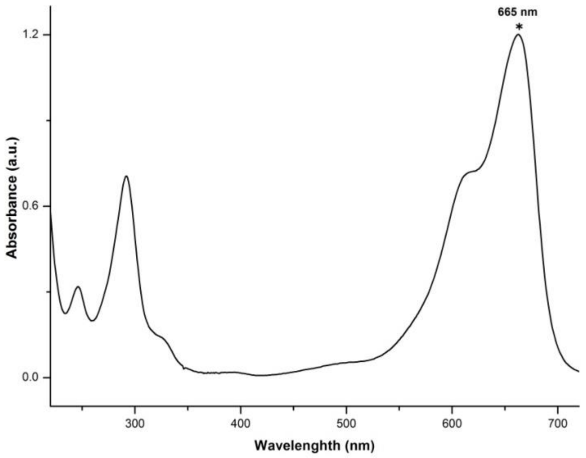

Fig. 3. Typical UV-Vis spectrum of methylene blue solution

Table. 1 Concentration of MB solution after adsorption tests

Sample	Dye concentration of the solution (mg/L)		Dye removal percentage (%)	
	Protocol		Protocol	
	A	B	A	B
K.	78	48,6	68,8	80,56
K.350	70,72	38,4	70,72	84,64
K.500	117,8	42,8	52,88	82,88

Electronic spectroscopy. UV-Visible spectroscopy was used to assess the adsorptive properties of the three clay samples by analizing the maximum adsorption peaks of MB, comparing them to the standard solution and calculating the amount of dye removed. In Fig. 3 is illustrated the adsorption spectrum of methylene blue, where the characteristic maximum peak is clearly visible at 665 nm [26]. Literature [27],[28] has shown that the parameters which influence the amount of dye that is adsorbed is the initial concentration of the colorant, the contact time between adsorbant and adsorbate, pH of the solution, the stirring speed and temperature of the mixture, among others. Our study focuses on effect of varying two of the parameters of the experiment on the quantity of methylene blue removed from the solution, which is the calcination temperature of the clay and the contact time between adsorbant and adsorbate. Characteristic bands which are attibuted to dimers, trimers and the protonated monomer of methylene blue, that appear at higher concentrations of the dye solution, can also be observed in the visible spectrum [29] but the most important band is the one attributed to the monomer, found at 665 λ (nm).

As shown in Table.1, the thermal treatment of kaolin does have an effect on its adsorption capacity, enhancing it. There is also a difference in the concentration of the solutions between the ones treated with clay for a total period of 5 hours and the ones which were in contact for 7 h. The MB removal percentage from the solution was considerably more significant in the case of Protocol (B), suggesting that contact time is important in obtaining the best adsorption results. A noticeable change is also evident among the un-calcinated sample and the ones subjected to heat treatment. In the cases of both Protocol (A) and Protocol (B), the dye removal percentage increased from the K. sample to K.350 and then decreased for K.500. The increase is most likely due to the loss of the water contained in the crystal structure of the clay which takes place with heating the sample. However the changes that can occur in the structure of clays, like the loss of the structure's crystallinity which has been observed for K.500, is known [30] to affect their adsorption properties of both organic and inorganic ions. This change is probably responsible for the lower level of dye retention of K.500 sample, as opposed to K.350.

4. Conclusions

The present study investigated the changes that calcination imposes on the methylene blue adsorption characteristics of Romanian kaolin clay. The clay was heat treated at 350°C and 500°C, the characteristics of the samples were investigated using FTIR spectroscopy and XRD and, in both cases, the indicative maximums for this type of clay material were identified. The most evident modifications that kaolin suffered with increasing the calcination temperature is the loss of water from its structure and the tendency towards becoming amorphous. Two work protocols were also employed, one that consisted in a total contact time of 5h between adsorbant and adsorbate and another one where the total contact time was of 7h. The UV-Vis analysis of methylene blue solution before and after adsorption studies which were carried out show that kaolin is an efficient adsorbent, K.350 sample removing the largest quantity of dye from the sollution, followed bt Ka and K.500. Differences were observed bewteen the work protocols, a higher contact time between clay and methylene blue solution improving the percentage of dye removed. Overall, we consider that heat treatment is an efficient method of improving the adsorptive characteristics of natural Romanian clay and that this material is a viable choice to become a universally used, economical and environmentally friendly adsorbent.

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*Corresponding author: alexandra.iordan@uaic.ro