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Adsorption of Humic Acid onto Kaolinite Clay: A Mini-Review

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ABSTRACT

Kaolinite clay has low cation exchange capacity and a small surface area. It has rarely been used as an adsorbent. In addition, it is green, low cost and efficiently adsorbent, which is a requirement for. Modification of kaolinite is necessary, to improve its adsorption capacity. Jordanian kaolinite has been modified by humic acid (HA) through a batch adsorption mode. The effect of HA concentration, pH and the temperature of solution were considered. HA adsorption becomes higher at low concentration, decreases with increasing pH and increases with solution temperature. Well characterized modified kaolinite shows good and strong interaction with HA, enhancement in its surface and charge structure, and an increase in the average pore radius. Therefore, it increases its reactivity and adsorption sites, especially towards heavy metal ions.

Keywords: Kaolinite, Humic acid, Batch adsorption, Adsorption capacity

INTRODUCTION

Kaolinite is a 1:1 aluminosilicate comprising a tetrahedral silica sheet bonded to an octahedral sheet, through the sharing of oxygen atoms between silicon and aluminum atoms in adjacent sheets [1]. The tetrahedral sheet carries a small permanent negative charge, due to the isomorphous substitution of Si4+ by Al3+, leaving a single-negative charge for each substitution [2]. Both the octahedral sheet and the crystal edges have a pH-dependent variable charge, caused by protonation and deprotonation of surface hydroxyl (SOH) groups [3]. Thus, the intensive interaction between kaolinite and humic acid (HA) is primarily controlled by surface acid-base properties. Kaolinite clay has seldom been used as an adsorbent, due to its low cation exchange capacity and small surface area [4,5]. Modification of clay minerals can be achieved either by impregnation or grafting of organic/inorganic molecules onto its surface [6]. Jordanian HA-kaolinite complex is made to improve the adsorption capacity of clay minerals. However, there is a dearth of information on the modification of kaolinite clay with HA and the effect of some variables on its adsorption capacity.

HAs are complex aggregates of dark-colored amorphous high molecular weight substances extracted from the natural degradation products of plant and animal residues [7,8]. Although considerable work about HA exists; only some have dealt with HA adsorption on clay minerals, because HA solubility increases with increasing pH [9,10].

Several studies have confirmed the potential of natural kaolinite for the adsorption of metal ions from solution. Moreover, several studies have been done to enhance the adsorption capacity of kaolinite. Saada et al. [11] investigated the influence of HA on arsenic retention: A crude, purified, Ca-exchanged kaolinite and two samples of HA-kaolinite were examined. HA-kaolinite was also used to adsorb the rare earth elements [12], uranyl ions [12] and phenanthrene [13].

Well characterized humic substances were adsorbed from aqueous solution onto Na-kaolin clay [14]. Some results demonstrate that adsorbed HAs play an important role in the deposition of polycyclic aromatic hydrocarbons in a soil environment. The distribution behavior of pyrene on HAkaolin complexes was also studied [15].

Several mechanisms are involved in the adsorption of HAs by kaolinite, the main ones being that the adsorption affinity increases with decreasing pH, thus indicating the importance of electrostatic interaction. The hydrophobic interaction and/or H-bonding also play a role. HA adsorption occurs via OH groups on the edge faces and basal octahedral faces (both positively charged), plus some adsorption at Si-O group, at certain pH values [16].

The adsorption of HA on kaolin has been studied at various

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conditions of initial solution pH and ionic strength and solidto-liquid ratio, equilibrium isotherm and thermodynamic studies were performed [17]. Few studies have addressed the effect of HA on particle surface characteristics, floc recoverability and fractal structure of alum-kaolin flocs [18]. Its physical and hydrodynamic properties have also been investigated at different HA concentration [19].

Many researches have been conducted to investigate the effect of adsorption of some heavy metals on kaolin, in the presence and absence of HA at various conditions [20]. The competitive adsorption equilibrium isotherms of Cu (II) and Cd (II) on kaolin have been measured [21]. Another approach was to compare the capacities of HA and fulvic acid to adsorb Cu (II) [22].

Jordan has huge reserves of kaolinite [23-25]. On the other hand, the gravest environmental challenge that Jordan faces today is scarcity of water. In addition, water in Jordan has been polluted by different types of pollutants, such as heavy metals.

This mini-review seeks to introduce modified Jordanian kaolinite clay by HA, as a new low-cost and more efficient adsorbent. The adsorption isotherm of HA on kaolinite clay will be studied at different pH and temperatures, in order to understand its nature, structure, behavior and properties. It is hoped to create a new adsorbent that can contribute to the solution of water pollution, which is a major problem in the world today.

EXPERIMENTAL METHOD

Kaolinite clay samples were crushed and sieved to particle size >250 μ m and then the clay fractions were subsequently exchanged with K⁺ ions, by washing them four times with 0.5 M KCl solution. The excess KCl was removed by repeatedly washing with deionized water until negative Cl⁻ was determined by AgNO3 solution. The clay suspensions were quickly frozen, freeze-dried and stored in closed containers prior to use [26].

A batch adsorption method was used for the preparation of the HA-Jordanian kaolinite complex samples. A 1000 (mg/L) of HA was prepared by dissolving 1.0 g \pm 0.1 mg of HA in 1.0 L of 0.01 M NaOH solution. An accurate mass $(0.04 \text{ g} \pm 0.1 \text{ mg})$ of kaolinite clay, measured to the nearest 0.1 mg, was shaken with 20.0 mL of 10, 30, 50, 70, 90, 110, 130 and 150 (mg/L)) solutions of HA for 24 h at 25, 35 and 45°C and pH=4.0, 5.0 and 6.0. The solution was adjusted by 0.10 M HCl and/or 0.10 M NaOH to the desired pH. Aliquot of the solution was then filtered and analyzed by a UV-VIS spectrophotometer, in order to measure the concentration of free HA. Two types of HA were used: commercial from Fluka company (FHA); and natural extracted from King Talal Dam (KTD). The maximum absorbance in the visible spectral range was at λ =320 nm for FHA and λ =215 nm for KTD-HA. Two types of modified kaolinite clay (MKC) complex were prepared: FHA-kaolinite clay (FHA-K); and KTD-kaolinite clay (KTD-K).

RESULTS AND DISCUSSION

Adsorption of humic acid into kaolinite clay

HA adsorption decreases with increasing pH (Figure 1), in a manner typical of 'ligand-like adsorption'. Both the adsorbent surface and the HA lose their protons as pH increases and becomes negatively charged: and consequently they repel each other. On the other hand, because both kaolinite clay and humate are in a hydrogenated form at low pH, the uncharged surface functional groups of the kaolinite surface and HA may attract each other via these protons and the electronegative O atoms, probably in the form of H bonds and thus HA reacts with the silanol and aluminol groups on the surface of the kaolinite [27].



Figure 1. Percentage of FHA adsorbed by kaolinite clay at 25°C and different pH versus the initial FHA concentrations.

The percentage adsorption of the HA on kaolinite clay, as a function of temperature, is also studied. It can be concluded that the adsorption of HA increases with an increase in the solution temperature more [28].

Characterization of MKC

Fourier transform infrared (FT-IR) spectroscopy: The IR data shows the kaolinite characteristic peaks: The OH stretching vibrations [29]; Si–O stretching vibrations; and the Si–O–Si and Si–O–Al lattice vibrations [30]. While other bands that appear refer to Al–O–Si deformation and Si–O–Si deformations [28].

Thermal properties: Figure 2 shows the thermal reactions of kaolinite. These reactions include dehydration of adsorbed water at T<150°C; dihydroxylation, followed by the transformation of the kaolinite to a metaphase and the recrystallization of the meta-phase into a crystalline phase (in the range of 400-650°C).



Figure 2. TGA thermogram of both unmodified clay and modified Jordanian kaolinite clay.

This thermogram shows a sharp drop for un-MKC, after about 500°C, while a less sharp drop for MKC. This may indicate that there is a slight increase in the thermal stability of MKC. While the residual mass percentage at 1000°C is equal to 88.07%, 91.71% and 91.92, for un-MKC, FHAkaolinite clay and KTD, respectively, this could indicate the more thermal stability of MKC, which is calculated at 3.64 for FHA-kaolinite clay and 3.85 for KTD-kaolinite. This is due to the presence of HA and the loss of crystalline water that decreases with modification. The thermogram shows a small drop at T<150°C for un-MKC, which represents release of the absorbed water in pores and on the surfaces. However, it is absent in MKC, which means that the kaolinite adsorbed HA with the release of water molecules. This is a good indicator of the presence of HA in the MKC.

Given that HA is an easily thermodegradable molecule, completely degraded between 400 to 600°C [31,32], its adsorption leads to a small increase in the thermal stability of modified Jordanian kaolinite clay.

Scanning electron microscope (SEM): SEM results observe that the surface topography of un-MKC consists of pseudohexagonal crystals. These crystals are typically thin and flexible plates. Distributed pores and a plate-like structure with high crystallinity and a high degree of ordering are also noticed, while the MKC shows that aggregation of HA particles occurs mainly as elongated layers and bundles of fibers, forming a relatively open structure. On the other hand, these fibers tend to mesh into a network to yield a sponge-like sheet with homogeneous grain distribution [28].

The adsorption efficiency of humic substances is related to the pore size of the adsorbent. According to literature reports, a 50-200 μ m pore size of adsorbent is suitable for the adsorption of humic substances [33]. The pore size of the kaolinite clay, used in this study by a Mercury Porosimetry Analyzer, was determined to be between 4.3 to 224.2 μ m and it was effective as an adsorbent for the adsorption of the humic substances.

Energy dispersive X-ray spectroscopy (EDS) of un-MKC and MKC: There is a clear difference between the EDS analysis of un-MKC and the others modified by HAs, for example, the appearance of new elements C and N due to the HA, which resulted in a decrease in the percentage of O and Al. The exact composition of HA varies from one source to another. The percentage of oxygen in KTD-K is less than FHA-K, while the percentage of nitrogen is higher, which may be due to degradation of dead organic matter in the dam [28].

Surface area and porosity of un-MKC and MKC:

Gas adsorption isotherms: The surface area was measured by gas adsorption, according to the Langmuir surface area method. N_2 gas can only capture or fill the micro and meso pores. According to Table 1, the un-MKC has a large number of pores in the range of micro and meso size and also 'small size pores'. There is a very important reason for the modification of kaolinite clay by HA. The MKC has a smaller number of pores with a small diameter range, due to HA adsorption.

Mercury porosimetry: Mercury Porosimetry [34] is suitable for the meso and macro pore range and it is used for large pore diameter analysis. **Table 1** summarizes the measured total porosity of the clays using this analyzer instrument.

Table 1. Langmuir calculated surface area and total porosity

 percentage of both unmodified and modified Jordanian

 kaolinite clay.

Type of clay	Surface area (m ² /g)	Total porosity (%)
Unmodified kaolinite clay	33.5	3.4
FHA-kaolinite clay	12.8	5.6
KTD-kaolinite clay	15.8	4.2

To summarize briefly these findings: The surface area is the highest for un-MKC and the initial increase of the HA content leads to a rather rapid decrease of the surface area of the modified kaolinite samples. However, a further increase of the HA content drastically reduces the amount of adsorbed N2 gas. Therefore, with an increase of concentration, the distribution of organic particles on the kaolinite surface changes. At the first stage 'new' parts of the kaolinite surface are covered, but then the HA builds a 'thicker' structure and this is deposited on parts of the surface already covered.

It can be concluded that the subsequent increase of HA content has a slight effect on the average pore radius. Obviously, the bonding of humic substances by mineral components of clay can change their organization and structure. At low HA concentration, it can be expected that the adsorption of HA on kaolinite particles can lead to flocculation of this mineral [35,36]. With an increase in the

HA amount, formation of steric (e.g. honeycomb), bigger floccules or aggregates and creation of new pores occurs. Still further increases of HA content may lead to a blocking of the pores, which have been already formed during flocculation. Thus, changes in porosity may be interpreted as the result of interplay between the formation of new pores (flocculation and aggregation) and the blocking of pores caused by adsorption. These changes concern wider pores, macro and meso pore. Eventual changes in very fine pores are out of mercury intrusion detection range. The same results were obtained by Sokołowska and Sokołowski [37]. They found that changes in the surface properties of the samples of kaolin amended with different amounts of HA are not proportional to the amount of HA added. The surface fractal dimension is the highest for untreated kaolin and it attains a minimum for samples with a small amount of HA added and smoothly increases to a constant value [37]. A small amount of HA deposited on a kaolinite surface blocks the narrowest pores, in which N₂ gas is strongly adsorbed. The addition of HA causes the pore size distribution to become narrower, but further changes of porosity with HA are small. These pores cannot be detected by mercury porosimetry measurements. The values evaluated from mercury intrusion measurements are lower than those calculated from N₂ gas adsorption data. Furthermore, due to the effect of HA deposition, wider pores and accessibility to mercury becomes narrower. The higher values of the surface area (determined from N2 gas measurements), than the values obtained from mercury intrusion data, indicate that finer pores, which can be penetrated by N₂ gas, are more geometrically heterogeneous than wider pores accessible to mercury.

These results approve that FHA-kaolinite clay has a larger number of large pores diameter than KTD-kaolinite clay. This means that kaolinite clay has absorbed FHA more than KTD-HA. This is supported by results obtained by EDS analysis, where the percentage of oxygen in KTD-K is less than FHA-K.

MKC is better for the adsorption of heavy metal ions, especially in hydrated form, than in an unmodified one. Finally, it is worth mentioning that this prepared HA-kaolinite clay has been examined to adsorb some heavy metal ions from an aqueous solution [38].

CONCLUSION

Modification of kaolinite clay with HA is needed, in order to enhance its adsorption capacity towards metal ions. HA adsorption decreases with increasing pH, and a decrease in the temperature of the solution. Several characterization methods support that kaolinite can adsorb HA. A TGA thermogram shows more thermal stability of MKC over the unmodified one. The total porosity of modified kaolinite is increased. Therefore, there are increases in its reactivity and adsorption behavior.

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