Synthesis and Properties of Different Types of Organomodified Montmorillonite for Contaminants Adsorption

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Abstract – This research gives a general overview of the microstructure, adsorptive characteristics, and environmental applications of the organomodified montmorillonite based adsorbents. Discussed new ways of developing clay mineral based adsorbents for target contaminants, and on the other hand can give a proper example to systematically show the various mechanisms for the uptake of contaminants on adsorbents.

Key words – montmorillonite, adsorption, organoclay synthesis, environment remediation, contaminants.

I. Introduction

Clay minerals and their modified derivatives have composed a large family of adsorbents which can be used for the adsorption of most of the chemical contaminants from aqueous solution. Among this family of adsorbents, those based on montmorillonite (MMT), a typical 2:1 type clay mineral, have been most extensively studied.

Adsorption has long been considered as a highly efficient approach for pollution control. Various adsorbents have been developed for the removal of contaminants from wastewater, polluted air and soil. One may say that most (if not all) of the contaminants can find proper adsorbents for their environmental remediation. For example, the adsorbents used for heavy metal cations include resin, metal (oxyhydr)oxide, zeolite, clay minerals, biosorbents, etc. [1]. Among the various adsorbents, clay minerals and their derivatives have composed one large family which are in contrast to other adsorbents such as activated carbon, zeolite, and resin in terms of the microstructure, adsorptive characteristics, and environmental applications. This large family of adsorbents, therefore, are drawing wide concerns nowadays.

II. Types of modification

Organic modifiers can alter the surface structure and environment of clay minerals, which then can enhance the affinity of the resulting materials (i.e., organoclays) toward organic contaminants. Generally, organomontmorillonite (OMMT) can be divided into three types according to their synthesizing methods and molecular structure of the modifiers. Type I are those synthesized with small rigid organic cations (e.g., tetramethylammonium (TMA), crystal violet, methylene blue). Type II are those synthesized with organic cations containing at least one long alkyl chains (i.e., cationic surfactants), such as hexadecyltrimethylammonium (HDTMA). Other less typical OMMT, which may be synthesized using special organic modifiers (e.g., nonionic/zwitterionic surfactants, cationic polymers, organosilanes, chelating reagents), or using more than one type of organic modifiers (e.g., surfactants + polymers, small organic cations + cationic surfactants), can be categorized into type III.

III. Type I

For type I OMMT, both experimental and molecular modeling studies showed that the small rigid organic cations (e.g., TMA) act as pillars, propping the silicate layers apart. As such, type I OMMT have porous structure, with a relatively high SSA. For example, TMA-MMT typically has a SSA of 100–300 m^2/g, depending on the layer charge of MMT and loading level of TMA [2]. Water saturation generally will not cause layer expansion of type I OMMT, as long as the remaining unexchanged inorganic cations are not extensively hydrated.

The intercalated organic cations may have special interactions with organic contaminants, e.g., π–π interaction and cation–π interaction, which then can further enhance the adsorption capacity of type I OMMT [3]. Thanks to the π–π interaction, benzyltrimethylammonium-MMT always has better adsorption capacity toward aromatic contaminants than TMA-MMT, although TMA has smaller molecular size. The hydrophobicity of organic cations can affect the adsorption capacity as well; the OMMT synthesized using less hydrated organic cations (e.g., trimethylphosphonium) may be better adsorbents than those synthesized using more hydrated cations (e.g., TMA). Compared with activated carbon, type I OMMT in general have weaker adsorption capacity because of their relatively smaller SSA. Several methods have been developed to increase the SSA and the adsorption capacity, e.g., reducing the layer charge of MMT [4], using novel approaches to synthesize reduced-charge OMMT. However, the obtained SSA is still less than 300 m^2/g in most cases, much smaller than that of activated carbon. As such, a large gap still exists in terms of enhancing the adsorption capacity of type I OMMT.

IV. Type II

With respect to type II OMMT, their interlayer space is commonly being fully occupied by the intercalated cationic surfactants, and thus they have a low porosity and a small SSA (in the order of several m^2/g). However, water molecules may cause layer swelling and change the interlayer structure of type II OMMT when they are dispersed in aqueous solution [5]. Recent molecular modeling studies provided detailed insight to the interlayer structure of type II OMMT, which clearly showed the presence of both surfactant aggregates and water dominated zone within the interlayers of HDTMA-MMT. In addition, a large portion of the siloxane surface of MMT was occupied by HDTMA [6]. With increasing loading level, cationic surfactants will occupy more of the interlayer spaces, forming larger surfactant aggregates and expelling water molecules out of the interlayer; the packing density of these surfactant aggregates will increase accordingly.

In addition to HOC, type II OMMT has been used for the uptake of various anionic contaminants as well, which include acidic herbicides and pesticides, anionic dyes, oxyanions, anionic radioactive nuclide, etc [7]. In general, relatively high loading level of cationic surfactant (e.g., over 1.0 time of the CEC of MMT) is necessary, as in this case a portion of surfactant will be loaded on type II OMMT as molecular form containing counterbalance anions, which serve as exchangeable anions in the uptake of anionic contaminants.

V. Type III

As a wide variety of organic modifiers were used to synthesize type III OMMT, their microstructure and adsorptive characteristicswill be quite different accordingly. Similar to the other two types of OMMT, the SSA of type III OMMT should be reversely related to the molecular size and loading level of the organic modifiers; organic phases may be formed when large organic modifiers were used for the synthesis [8]. On the other hand, as some of the organic modifiers contain functional groups, the resulting OMMT may have special interactions with contaminants [9]. Also, a wide variety of polymers have been used to synthesize type III OMMT, which then have been applied for the uptake of HOC, anionic dyes and heavy metal cations.

Cationic surfactants have been used to intercalate MMT with other organic modifiers (e.g., cationic polymer, cationic dyes) to synthesize type III OMMT. As the arrangement of cationic surfactants within the interlayers of MMT can be adjusted by the co-intercalated organic cations, the resulting type III OMMT then may have better capacity in uptaking HOC than the corresponding type II OMMT, with partition generally being the predominant mechanism.

To enhance the adsorption capacity of heavy metal cations, organic modifiers with particular functional groups (e.g., $-SH$, $-NH_2$, $-COOH$, $-CS_2$) that can specifically interact with heavy metal cations have been used to synthesize type III OMMT [10]. The results showed that the resulting OMMT had much better capacity than original MMT in the uptake of heavy metal cations. In addition, these OMMT also showed adsorption selectivity because of the special chelating functionalities, i.e., $-NH_2$ for Pb(II), $-SH$ for Pb(II) and Zn(II), $-COOH$ for Cd(II), and $-CS_2$ for Pb(II).

In general, type III OMMT have similar characteristics as type II OMMT in terms of uptaking HOC, and thus they share similar advantages and disadvantages. On the other hand, since cationic polymers generally have high charge density, type III OMMT can be quite suitable in uptaking anionic contaminants. As for the uptake of heavy metal cations, choosing proper organic modifiers (e.g., with special groups and low costs) is of high importance for the synthesis of type III OMMT.

Conclusion

A comprehensive survey of the numerous literatures shows that MMT based adsorbents have rather complicated structural and adsorptive characteristics. They may have porous or nonporous structure and contain various functional groups; their interlayer structure may be evidently affected by the incorporation of water molecules in aqueous medium. With the complicated structural characteristics, these adsorbents can be used for a wide variety of contaminants, including hydrophobic organic contaminants, cationic/anionic dyes, heavy metal cations, oxyanions, radioactive nuclides, etc. Accordingly, a wide variety of mechanisms are involved for the uptake of these contaminants, such as surface adsorption, partition, ion exchange, surface precipitation, and structural incorporation.

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