Green Remediation of Heavy Metal Polluted Water and Soil Using Clay Minerals: A Review

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Abstract. Among all natural minerals, the natural clay mineral has been widely used for environmental pollution treatment both in water and soil, especially heavy metal (HM) pollution in recent years. In this review, modified methods for clay minerals and their application for the remediation of HM contaminated water and soil are summarized. The remediation mechanisms of HMs in water and in soil by modified clay minerals were discussed. Moreover, the existing problems and development of clay minerals are also discussed.

1. Introduction

With the acceleration of economic development, environmental contamination has become a severe issue. Heavy metal pollution is one of the critical contaminated issues because of its poisonousness and abundance [1]. Heavy metals (HMs) in soil and water are accumulated by unreasonable disposal and extensive use of mine waste, sewage sludge, urban compost, fertilizers and industrial development without efficacious sewage control [2].

Heavy metals (HMs) pose a significant risk to humans and animals through the food chain [3, 4]. Faced with environmental contamination threatening the sustainable development of mankind, some technologies have been used to remove heavy metals (HMs) of wastewater and polluted soils, including chemical precipitation, ion exchange, absorption, electrochemical methods [5], biological treatment and solidification/stabilization (S/S). Among these technologies, adsorption and S/S have significant advantages for water and soil remediation.

Clay materials have become one of the fastest-growing pollution adsorption and S/S materials in recent years depending on their ability to deal with heavy metal (HM) contamination in water bodies and soils both economically and green. At present, clay mineral materials, such as montmorillonite (Mt), kaolinite, sepiolite, attapulgite, and so on have been extensively studied. However, the adsorption of single mineral materials for HM wastewater treatment has great limitations. The industrial application of clay minerals is limited by its crystal structure and negative charge [6]. Therefore, the modification of natural mineral materials has become a hot topic in the field of treatment for HM contamination. The modification of clays are mainly to prepare a new type of modified clay mineral material which has high physical and chemical stability, strong regeneration ability, better adsorption effect and performance than the original material. The modified materials can widely meet the treatment of different pollution sources, and promote the green recycling of clay mineral resources.
2. Types of natural clay minerals
Clays can be divided into amorphous and crystalline according to the difference of the inner layer structure. [7]. The crystalline clays can be further divided into several categories, like 1:1 type layer (kaolinite), 1:1 type tube (halloysite), 2:1 type layer (Mt, smectite, illite, vermiculite and beidellite), the regular mixed-layer (Chlorite group) and 2:1 chain-structure type (playgorskite and sepiolite) [8, 9]. In the treatment of HM pollution, mineral materials in the form of layers, chains, etc. have good processing performance.

3. Preparation and characteristics of modified clay minerals
There are various methods to improve the adsorption performance of clay minerals by different modifying techniques. Modified clay minerals are mainly divided into three groups: thermal modification, acid activation [10], and organic modification [11], according to different modification types. The following sections briefly summarize diverse modified clay minerals, such as their synthesis, performance, and application in the environment.

3.1. Thermal modification
Heat treatment refers to heating the raw clay minerals at the required temperature (200°C–1000°C) within a given period of time (mainly to 2-4 hours). [12]. Exposing clays to mild to moderate heat treatments can remarkably change the surface properties of clays [13]. Silicon and aluminum atoms in most clay mineral materials exist in crystalline form. The structure of this form in many clay mineral materials has strong stability. After thermal modification, the clay mineral materials lose surface water, change the pore structure and clean some impurities, increasing the specific surface area and adsorption capacity of clays. However, it is necessary to control the heating temperature, since too high temperature may break the clay structure. For example, the Mt layers collapse at 600 °C and 800 °C; however, that the ZrO₂-Mt composites (400 °C treated) have higher removal effectiveness indicates that higher temperature will destroy the Mt layer structure and diminish the adsorption capacity [14].

3.2. Acid activation
Acid activation is a treatment generally applied on clays with hydrochloric or sulphuric acid, to obtain new materials with better characteristics that are fit for new environmental applications [15]. When the original mineral material is in full contact with the modifier, certain substances of the material can chemically react with the acidic modifier. The interlayer bonding force of the material is reduced; mineral lattice structure of the layer state is changed; CEC is decreased [16]; specific surface area is increased [16]; pore volume and pore size of the clay mineral material are enlarged. Furthermore, the acid modifier can also undergo displacement reaction with the natural material, as H⁺ in the acidic modifier can displace cations (such as Ca²⁺, Mg²⁺, etc.) with a larger particle size in the material, and expand the ion exchange channel. However, the treatment of clay minerals with high consistency of acid will cause excessive leaching of Al³⁺ leading to the rupture of lattice structure, reducing the CEC and the specific surface area of clay minerals [17]. For the purpose of preventing these complications, a suitable acid consistency to obtain maximal adsorption ability for clay minerals was essential. Acid modification caused the Brunauer Emmett and Teller (BET) surface area (SBET) to increase from 55.76 to 96.48 m²/g, and the total pore volume (TPV) to increase from 0.0688 to 0.101 cm³/g which is beneficial for effective adsorption [18].

3.3. Organic modification
Organic modification is the process in which organic functional groups with strong adsorption effects on HMs are loaded on the surface or interlayer of inexpensive clay minerals. Organically modified clay minerals are used worldwide attributed to their advanced properties, like large surface areas and CEC. Most clay minerals are hydrophilic owing to hydrated cations in their interlayer space with little compatibility [13]. Organic modification can make clay minerals hydrophobic. For instance, in the
process of interaction between quaternary ammonium compounds with clay minerals, hydrated cations are exchanged with hydrophobic organic cations, thereby making the resulting clay hydrophobic [13]. Organic modification can reduce the sheet surface energy of clay minerals and increase affinity for HM ions, ultimately increasing the adsorption capacity of mineral materials for HMs. The modification method supported the –SH group on the surface of the Mt, removing the impurities covered inside and outside the pore, which was conducive to the stable adsorption of mercury [19]. Similarly, polyionenes are inserted into the interlayers of Na+-Mt causing the distance between adjacent layers to increase [20].

4. Application of modified clay minerals

4.1. Treatment of heavy metal ions in aquatic environments with modified clay minerals

Adsorption treatment of HM contaminated wastewater is a commonly used technology that is economical, efficient and environmentally friendly. Clay minerals have big surface area, high CEC and are general substances in the environment [21]. Clay mineral materials with good adsorption capacity towards various metal ions have become the main choice of adsorption materials due to their large reserves, excellent prices and good reproducibility.

4.1.1. Heavy metal removal in water by 1:1 type clay minerals. Kaolinite is a 1:1 type layer clay mineral. Kaolinite nanotubes (KNTs) have adsorption capacities of 103 mg/g, 116 mg/g, 89 mg/g, and 91 mg/g for Zn$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ and Cr$^{6+}$, respectively, which are definitely higher than kaolinite and carbon nanotubes (CNTs) adsorbents [22]. The CEC and specific surface area of geothite–humic acid (GHA)-modified kaolinite were 40 meq/100 g and 13 m$^2$/g, which was five times higher than that of original kaolinite [23].

Halloysite is another 1:1 type tube clay. Use halloysite clay, hexadecyltrimethylammonium bromide (CTAB) and cellulose to prepare clay-cellulose biocomposite (CCB) [24]. The maximal adsorption capacity of CCB for Pb$^{2+}$ and Cd$^{2+}$ was 389.78 and 115.96 mg/g, respectively [24]. Functionalized halloysite nanotubes with amino groups are used to absorb Pb$^{2+}$ ions [25]. The amino group promoted the Pb$^{2+}$ adsorption of Hal-NH$_2$, thereby improving its adsorption efficiency [25]. A magnetic Fe$_3$O$_4$/Halloysite nanohybrid (Fe$_3$O$_4$/HNTs@C) was prepared [26]. Fe$_3$O$_4$/HNTs@C had higher adsorption ability for Cr (VI) ions with adsorption capacity of 132 mg/L at 303K, which was about 100 times higher than pristine material [26]. The thermal modified serpentine which was heated at 700 °C, having the largest surface area and exhibiting the adsorption capacity of 15.21 mg/g, which was 2 times more than raw material [27]. The adsorption mechanisms were that the surface of serpentine mainly formed of CdCO$_3$ and Cd (OH)$_2$ precipitation [27].

4.1.2. Heavy metal removal in water by 2:1 type clay minerals. Sodium-montmorillonite (Na+-Mt) was modified to L-lysine monohydrochloride (L-Mt), and the maximal adsorption capacity of Pb (II) on the L-Mt up to 43.3 mmol/100 g, which was two times higher than that of Na+-Mt (up to 15.3 mmol/100 g) [28]. Improving the clay surface can enhance its metal adsorption capacity. It was found that surface modification by the cationic surfactant (Bencylhexadecyldimethyl ammonium chloride (BCDMACl)) was successful [29]. The modified bentonite exhibited the maximum adsorption capacities of 50.76 and 35.21 mg/g for Cu (II) and Zn (II), respectively, which were about 2.5 and 2.0 fold improvements over raw material [29].

Compared with pristine clay, Fe-Mt had a larger interlayer spacing with higher affinity for metal cations [30]. The sorption capacity of Na-Mt was increased in the order: Pb$^{2+}$ = Cd$^{2+}$ < Cu$^{2+}$ < Zn$^{2+}$ < Mn$^{2+}$ < Ni$^{2+}$ < Cr$^{3+}$ [31].

Cu$^{2+}$ ions enter the montmorillonite through exchangeable adsorption and specific adsorption [32]. The selective modification of Na$^+$-Mt surface with polyionene was followed by poly (succinimde-co-aspartate) [20]. The Langmuir model showed that the adsorption capacity of polyaspartate/Mt (IPS) for Pb$^{2+}$ and Cd$^{2+}$ was 92.59 and 67.57 mg/g, respectively, and the modification of Na$^+$-Mt enhanced their
adsorption capacity by about 87.91 and 29.84% for Pb$^{2+}$ and Cd$^{2+}$, respectively, attributed to inclusion of extra active sites of polyaspartate [20].

The zeolite NaY was prepared from rice husk ash (RHA) and the commercial zeolite NaY both modified with surfactants were used to remove chromate and arsenate anions from water with better adsorption capacity; whereas, the unmodified zeolite Y had little affinity for the Cr$^{6+}$ and As$^{5+}$ anionic species [33].

Sepiolite is a 2:1 type chain-structure type clay. The adsorption of Cu$^{2+}$ from water by pristine sepiolite (RS) and iron oxide-coated sepiolite (ICS) materials was studied, and the adsorption capacities of RS and ICS were 14.96 and 21.56 mg/g, respectively [34]. Attapulgite is also a 2:1 type chain-structure type clay. Raw attapulgite (APT) and struvite/attapulgite (MAP/APT) obtained from nutrient-rich wastewater treated by MgO modified APT, were used as absorbents to remove Cd$^{2+}$ from aquatic environment [35]. The Raw APT and MAP/APT exhibited maximal Cd$^{2+}$ adsorption capacities of 10.38 mg/g and 121.14 mg/g, respectively [35].

4.2. Treatment of heavy metal ions in soil by modified clay minerals

In recent years, clay mineral materials like Mt, sepiolite, and attapulgite have been applied to remediate HM contaminated soil due to their superior properties, huge reserves, and low price [36]. Stabilization mechanisms of clay minerals for HMs in soil comprise surface adsorption, ion exchange and co-precipitation [37]. The remediation mechanisms mostly contain precipitation, and sorption [36]. Considering the occurrence form of HMs in the soil determines the size of the biological hazard. Clay mineral materials can effectively achieve the transformation of HMs in soil occurrence forms from high toxic to less toxic form, showing considerable remediation effects.

4.2.1. Heavy metal remediation in soil by 1:1 type clay minerals. Clay minerals have the ability to immobilize toxic HMs. Lime activated the clay to produce calcium silicate hydrates and calcium alumina hydrates, which increased the degree of polymerization of clay hydrates, improving the mechanical property [38]. Owing to the dissipation of Ca (OH)$_2$ by as and Pb (i.e., inhibitory effects) and indigenous soil buffering capacity, a higher concentration of lime was required for sufficient hydration of clays in the soil S/S process [38].

4.2.2. Heavy metal remediation in soil by 2:1 type clay minerals. Mts modified with tetramethylammonium (TMA) and hexadecyltrimethylammonium (HDTMA) were synthesised for repairing Cr (VI) contaminated soils [39]. TMA modification increases surface area and pore volume of Mts, and both T-Monts and H-Monts could effectively stabilize the chromium [39]. The Mont-OR-SH was synthesised by grafting the thiol group (–SH) to the Mt which was modified by organic surfactant (Mt-OR) [19]. For two types of soils, with a stabilization time of 2 weeks, the stabilization efficiency of Mont-OR-SH was 91.7% and 96.7% which was higher than that of Mont-OR (60.4% and 82.4%) [19].

By using humic acid modified montmorillonite (HA-Mt), the content of HMs in agricultural soils co-contaminated by Cd and Hg can be effectively stabilized [40]. Compared with the pristine Mt, the addition of 5% HA-Mt could effectively decrease the leachate Cd and Hg contents by 69.5% and 65.9%, respectively, which both below the TCLP regulatory limits for non-hazardous waste [40]. The stabilizing effect of sepiolite on Cd pollutants in paddy soil has been confirmed by situ demonstration [41]. The cadmium concentration of 0.025 M HCl extractable cadmium content, and exchangeable cadmium content of paddy soil definitely reduced during the two years, which indicated that the immobilization effect could last for at least two years [41].

A pot study was conducted to evaluate the effect of sepiolite from 1% to 5% on cadmium solubility [42]. As the rate of sepiolite increased from 1% to 5%, the pH of the soil increased from 0.3 to 1.0 unit; similarly, cadmium content in acid soluble phase was reduced by 42.8% and added in the residual phase by 35.8% at 5% treatment [42]. Furthermore, the maximal cadmium adsorption capacity was 37.35 mg/g at 5% treatment compared to control which was only 12.23 mg/g [42]. A column leaching experiment
was performed to find out the effects of mercapto-palygorskite (MPAL) and mercapto-sepiolite (MSEP) on the leaching behavior and fraction distribution of HMs [43] the exchange fraction cadmium and carbonate-bound cadmium reduced after leaching [43].

5. Conclusions
At present, the treatment of HM pollution with clay minerals and their modified materials has reached a certain technical level. In practice, clay mineral materials have been accepted due to their economical and green recycling, but the researchers found some problems arising from the rapid development of treatment process: (1) Due to different types of current pollution sources and pollutants, the phenomenon of coexistence of multiple HMs in aquatic environments is often involved, but the research on adsorption materials is currently less involved in the competitive adsorption of multiple HMs, and therefore, the research on composite water pollution is still lacking; (2) Although, natural mineral materials are abundant in the world and are currently used as adsorbent materials to treat HM pollution in water and soil. The secondary utilization rate of materials is low, and its separation from the environmental medium after adsorption saturation is very difficult, thus easily causing secondary pollution; (3) The long-term effects of passivation, and the microscopic mechanism of clay minerals in remediation of HM contaminated soil should be further studied; (4) The research on soil fertility and structure using clay mineral materials as HM immobilizing agents in soil are relatively defective; (5) We should also study the clay minerals that are seldom concerned, and try to modify them to improve their properties, to explore new materials to repair pollution.

In the future, for the continuing of developing new mineral materials with the goal of low cost and high efficiency for clay mineral materials, it is recommended that the associated problems of treatments’ development process should also be considered and resolved, solve the derivative problems of the application of environmental materials in the field of HM pollution, expand the scope of application of modified clay mineral materials, and play a long-term role in the treatment of HM pollution by clay mineral materials.

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