Halloysite nanotube applications for heavy metals removal from wastewater

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Abstract. Halloysite is a clay mineral that it is found in nature being a non-toxic material. Halloysites are used in different industrial fields having an important potential. In this paper we reviewed the properties and structural characteristics of halloysites and their applications in wastewater treatment. Halloysites showed good results for heavy metals removal process from wastewater. Researches has been carried out on removing from wastewater heavy metals, such as: Cu(II), Fe(III), Cr(VI), Pd(II), Pb(II), Ag(I), Co(II), Zn(II).

1 Introduction

Halloysite nanotubes with negative charges on external surface represent a type of hollow tubular material measuring an outside diameter from 30 to 70 nm and an inner diameter of 20–30 nm [1, 2], which present excellent chemical and physical properties because of their abundant hydroxyl groups, large specific surface area, great biocompatibility and porous structure. Halloysite nanotubes are not toxic for humans [3, 4], so they are successfully applied for pharmaceutical and biomedical industries [5, 6] and have been applied in the adsorption process for dyes and heavy metals removal from wastewater [7–9].

Worldwide, in China, Australia, New Zealand, the United States, Brazil and Mexico have been found large deposits with halloysites [10]. Halloysite nanotubes have a length between the submicron scale and several microns, occasionally can exceed 30 µm [10], an outside diameter between approximately 30 and 190 nm, an inner diameter between almost 10 and 100 nm [11, 12].

2 General structure and principal properties of halloysite nanotubes

Halloysite nanotubes are aluminosilicate having the chemical formula $Al_2Si_2O_5(OH)_4 \bullet nH_2O$, n having value 2 or 0 in case of hydrated or dehydrated halloysite. At temperature and humidity ambient conditions or by moderate heating the hydrated state can change into the dehydrated state irreversibly. Halloysite nanotubes can have different appearances such as thin or stubby and long or short. Halloysite nanotubes have layered and well crystallized structure composed of silicon dioxide tetrahedra present in the external layer and aluminum oxide octahedra present in the internal layer [13].

The external area of halloysite nanotubes has different electrical and chemical properties from the internal area due to the particular crystal structures. The internal area has a positive charge and a large number of hydroxyl groups (Al–OH), whereas the external area has a negative charge and a lower density of hydroxyl group (Si–OH). Actually, the external area of halloysite nanotubes is especially occupied by groups such as Si–O–Si and has a minority of Si–OH groups displayed on the possible defects or margins of the sheets. Thus, the oxygen atoms powerful electronegativity gives to the external area a negative charge. Meantime, the hydroxyl groups lower density on the external area together with the charged properties provide halloysite nanotubes well dispersion capacity in nonpolar polymers, giving a lot of advantages for the halloysite nanotubes / polymer nanocomposites preparation. In addition, halloysite nanotubes are considered as materials of reinforcing and flame retardancy in case of halloysite nanotubes / polymer nanocomposites due to their high appearance ratio between length and diameter and their borders against heat and mass transport [14].

3 Halloysite nanotubes-derived applications for heavy metal ions removal

Halloysites have been found as excellent alternatives for the conventional adsorbants used for the metal ions (Pb (II), Zn (II), Cu (II), Cd (II), Co (II) and Cr (II)) removal from wastewater. The removal of heavy metal ions from domestic and industrial wastewater or even drinking water has an environmental importance for reducing water pollution. Natural halloysite nanotubes without modifications can eliminate heavy metal ions from wastewater by physical and/or chemosorption mechanisms, metal speciation, site geometry, etc. Nevertheless, for the increasing of the heavy metal ions loading capacity, the nanotubes of halloysite are coated with different nanoparticles or functional groups. In Table 1 are showed the halloysite nanotubes applications used in the heavy metal ions removal from wastewater. Due to the layer structure, natural halloysite nanotubes were interpolated with active molecules in order to increase the reusability and loading capacity. For instance, intercalated halloysite nanotubes with sodium acetate were developed at different contact time and this development shows that the most intercalated trial was the most efficient for Cu (II) removal from wastewater having an adsorption capacity of 50 mg/g. [15]

Table 1. Halloysite nanotubes derived application used in heavy metal ions removal process from wastewater.

Adsorbant	**Pollutant**	**Initial concentration (mg/L)**	**pH**	**Adsorption capacity (mg/g)**	**Ref.**
Halloysite nanotubes / alginate	Cu(II)	50-100	-	74.13	16
Halloysite nanotubes / CH_3COONa	Cu(II)	10-200	6	52.3	17
Halloysite nanotubes / CH_3COO^-	Cu(II)	10-200	6	~50	15
Halloysite nanotubes / HBA	Fe(III)	10	4	45.54	18
Halloysite nanotubes / HDTMA	Cr(VI)	25-300	3-10	6.61	19
Halloysite nanotubes / KH-792	Cr(VI)	0-400	2-9	37.25	20

Table 1. Halloysite nanotubes derived application used in heavy metal ions removal process from wastewater (cont.)

Adsorbant	Pollutant	Initial concentration (mg/L)	pH	Adsorption capacity (mg/g)	Ref.
Halloysite nanotubes / murexide	Pd(II)	1	1-7	42.86	21
Halloysite nanotubes / PPy	Cr(VI)	1000	2-11	149.25	22
Halloysite nanotubes / PSA	Pb(II)	1	1-7	23.58	23
Natural halloysite nanotubes	Ag(I)	~50	-	3-6	24
Natural halloysite nanotubes	Co(II)	10	3-11	~6	25
Natural halloysite nanotubes	Zn(II)	10	2-9	9.87	26

The abbreviationsare: HBA - 2-hydroxybenzoic acid; HDTMA - hexadecyltrimethylammonium bromide; KH-792 - *N*-β-aminoethyl-γ-aminopropyl trimethoxysilane; PPy – polypyrrole; PSA - *N*-2-pyridylsuccinamic acid.

In order to remove Cr(VI) from wastewater was synthesized a polypyrrole-coated halloysite nanotubes nanocomposite through *in situ* polymerization process of pyrrole on halloysite nanotubes. The maximum removal capacity was 149.25 mg/g at pH 2 and 25 °C temperature. Nanocomposite was used for three cycles without loss its adsorption efficiency [22]. Besides removal capacity, the adsorption rate is also an important factor for the halloysite nanotubes adsorbants evaluation. In order to improve the adsorption rate for Cr(VI), was synthesized a new halloysite nanotubes - based adsorbant coated with the surfactant hexadecyltrimethylammonium bromide. Thus, the modified halloysite nanotubes showed an excellent adsorption for Cr(VI) reaching a maximum removal capacity of 90% in 5 minutes [19].In other articles, the adsorption properties of natural halloysite nanotubes were investigated for Ag [24], Co [25] and Zn [26] ions removal from wastewater.

Conclusions

Halloysite nanotubes - derived adsorbants presented excellent advantages such as reusability, easy operation, non-secondary pollution and lower cost in comparison with chemical methods for heavy metal ions removal.

Functionalized halloysite nanotubes proved a higher adsorption capacity (6.61–149.25 mg/g) for heavy metal ions than natural halloysite nanotubes (less than 10 mg/g), which is showed in Table 1.

Thereby, halloysite nanotubes are materials that have interesting properties being promising and cost-effective and it can be used in the composition of functional organic/inorganic nanocomposites. Halloysite nanotubes - derived properties can guarantee the wastewater treatment.

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