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Removal of malachite green by adsorption and precipitation using aminopropyl functionalized magnesium phyllosilicate

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ABSTRACT

We report a method for the removal of malachite green (MG) by adsorption and precipitation using nano-sized aminopropyl functionalized magnesium phyllosilicate (AMP) clay. MG, which is used in aquaculture and fisheries, is a carcinogenic and mutagenic compound. In response to these health risks, many efforts have been focused on adsorption of MG onto various adsorbents, which is a versatile and widely used technique for removing MG from water. Herein, we describe the adsorption and precipitation of MG using AMP clay, as well as the alkaline fading phenomenon of MG. In this study, prepared AMP clay and the precipitate product after the reaction of MG–AMP clay mixture were characterized. In addition, adsorption isotherms and kinetics, as well as thermodynamic studies are presented. Based on the results, we suggest a macro- and microscopic removal mechanism for the adsorption and precipitation of MG using AMP clay. An AMP clay dosage of 0.1 mg mL^{-1} exhibited a maximum removal capacity of 334.80 mg g^{-1} and 81.72% MG removal efficiency. With further increases of the AMP clay dosage, removal capacity by AMP clay gradually decreased; at dosage above 0.2 mg mL^{-1} of AMP clay, the removal efficiency reached 100%.

1. Introduction

Malachite green (MG) is a basic dye that has been used for dyeing wool, silk, leather and cotton as well as a fungicide and ectoparasiticide in aquaculture and fisheries it is generating environmental concerns [1]. Not only the colors of the dyes affect the penetration of sunlight into streams, but also the dye is carcinogenic and mutagenic [2,3]. Due to the considerable resistance of MG to biodegradation, physical and chemical processes for MG removal have been widely studied. Characteristics of the removal procedures that have been investigated include removal capacity, treatment cost, and operating conditions, among other factors [4–6]. Chemical treatment technology is costly and involves complex processes that generate toxic by-products [7]. Therefore, alternative physical methods for MG removal have been widely studied. Using low cost adsorbents of silica based materials, such as clay and its derivatives, may be a good approach because of their large surface area and high cationic exchange capacity [8,9]. Other adsorbents, such as ash [10], chitosan [11], cyclodextrin [12], activated carbon [13,14], hen feathers [15], plant leaves [16], chlorella [17], de-oiled soya [18], and algae [19], have been successfully evaluated with regard to their ability for physical removal of MG. However, many of these studies have not considered the alkaline fading phenomenon of MG. Recently, Samiey and Toosi detailed the MG alkaline fading phenomenon [20–22], and specifically reported that cationic chromatic MG was changed into a white precipitate carbinol base at an alkaline pH. As shown in Fig. 1, three forms of MG can exist; leuco MG is formed when MG penetrates into the human body. However, we will consider only chromatic MG and MG carbinol base, which is MG form in alkaline pH condition in aqueous systems. When MG is removed by adsorbents under an alkaline solution, the MG carbinol base in precipitate form should be considered [22]. More recently, clay minerals of layered organo-inorganic hybrid materials, resembling the talc parent structure $Si_8Mg_6O_{20}(OH)_4$, have been synthesized by a sol–gel reaction at ambient conditions with various combinations of metal ions, such as magnesium [23,24], nickel [25], and zinc [26]. Organo-functionalities of above clays have been extensively investigated from an academic as well as an applied perspective. Mann and colleagues further synthesized organoclay (AMP clay) as 2:1 trioctahedral typed aminopropyl magnesium (organo)phyllosilicate. AMP clay can be synthesized by a one-pot sol–gel reaction in ambient conditions by controlling centered metal ions and sandwiched organo-functionalities [27,28]. This process results in organo-building blocks that are optically transparent due to the repulsion of protonated amine groups in aqueous media. The cationic and water-solubilized properties of AMP clay in aqueous solutions have been utilized to construct hybrid

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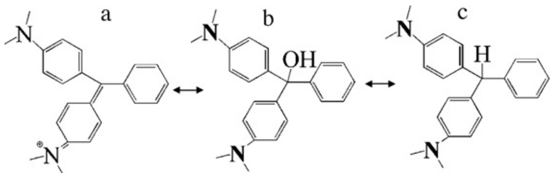

Fig. 1. Three forms of malachite green (MG): chromatic malachite green (a), carbinol base (b), and leuco malachite green (c).

materials with biomolecules [29–32] and Schiff bases [33], dye labeling for cellular uptake [34], and drug delivery systems [35].

Unfortunately, artificial AMP clays have not been applied toward pollutant clean-up, even though their cationic and ammonium properties in aqueous solutions merit the feasibility of such an approach. Herein, we report, for the first time, the adsorption and precipitation of MG using the positively charged organo-building blocks of nano-sized AMP clay sheets. The specific goals of this study were (1) to prepare and characterize AMP clay and the MG–AMP clay mixture, (2) to suggest a removal mechanism that includes adsorption, precipitation, MG fading, and collapsing of the AMP clay structure, and (3) to present the adsorption kinetics and a thermodynamic study of the MG–AMP clay mixture.

2. Experimental

2.1. Materials

The cationic dye, MG oxalate (C.I. Basic Green 4, C.I. Classification Number 42,000, $C_{52}H_{54}N_4O_{12}$, M.W. = 927.00, λ_{max} = 617 nm) and 3-aminopropyltriethoxysilane (APTES, 99%) were supplied by Sigma–Aldrich (St. Louis, MO, USA) and used without further purification, unless otherwise specified. Ethanol (>99.9%) was purchased from Merck KGaA (Darmstadt, Germany). Magnesium chloride hexahydrate (98.0%) was obtained from Junsei Chemical Co. Ltd. (Tokyo, Japan). HCl or NaOH (1.00 M or 0.10 M) standard solutions were purchased from Dae Jung Chemicals (Shiheung, Korea) to adjust the final pH of samples.

2.2. Preparation of AMP clay

For AMP clay preparation, we followed methods that have been previously reported in the literature [30,31,34,35]. Specifically, magnesium chloride hexahydrate (0.84 g) was dissolved in 20 g of ethanol and 1.3 mL of APTES added to this solution, where the intended molar ratio of Mg to Si is 0.75, with continuous stirring. A white colored precipitate gradually formed within 10 min and was stirred overnight for the reaction to reach completion. The

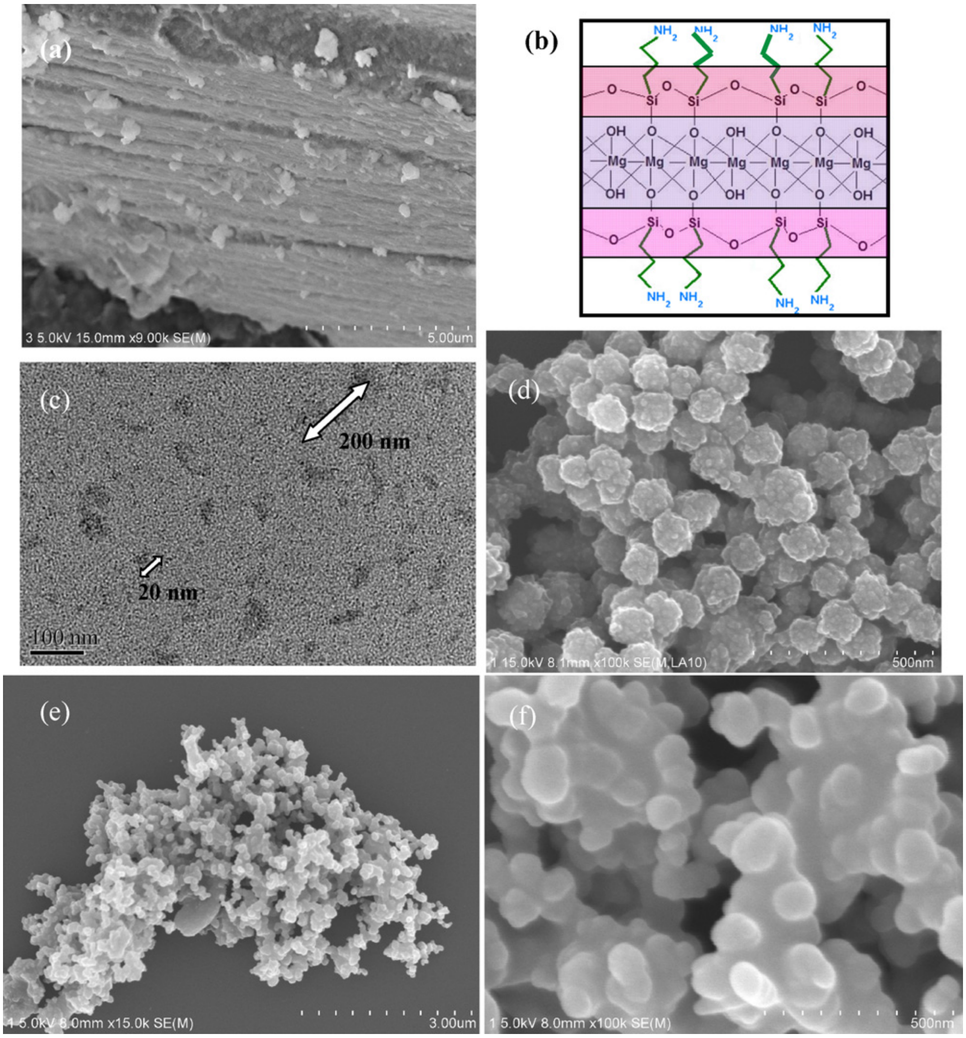

Fig. 2. SEM/TEM images of AMP clay and precipitate of MG–AMP clay mixture. (a) SEM image of powder AMP clay, (b) a schematic unit structure of AMP clay, (c) TEM image of diluted AMP clay sheets in aqueous solution on carbon-coated copper grid, (d) SEM image of the precipitated carbinol base, and (e) SEM images of low magnification and (f) high magnification of MG–AMP clay mixture.