



Highly efficient and selective adsorption of malachite green onto granular composite hydrogel

Yian Zheng^a, Yongfeng Zhu^{a,b}, Aiqin Wang^{a,*}

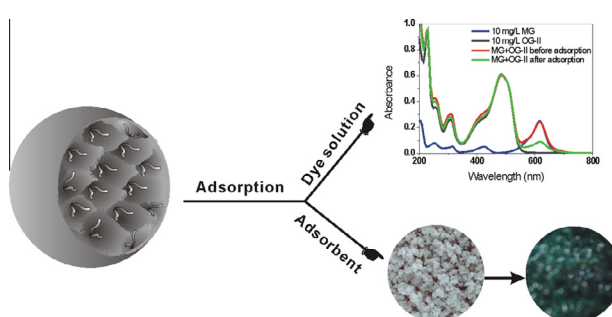
^aCenter of Eco-Materials and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- 3D structured composite hydrogel can be obtained in the form of granules.
- The hydrogel can be prepared at room temperature and atmosphere conditions.
- The hydrogel shows fast, high and pH-independent adsorption properties to MG.
- The hydrogel shows excellent adsorption selectivity for cationic dyes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 1 June 2014

Received in revised form 7 July 2014

Accepted 8 July 2014

Available online 17 July 2014

Keywords:

Granular

Composite hydrogel

Redox initiator

Malachite green

Adsorption

ABSTRACT

A series of granular composite hydrogels were prepared at room temperature and atmospheric oxygen via a facile in-situ polymerization using chitosan as the grafting backbone, acrylic acid (AA) and itaconic acid (IA) as the monomers, and attapulgite (APT) as the inorganic component. The resulting AA-IA-APT hydrogel is well characterized to possess a three-dimensional structured polymeric network and can be used for the adsorption of malachite green in single or mixed dye solution due to its anionic characteristics. The introduction of a small amount of APT (5 wt%) into the hydrogel can not only accelerate the adsorption rate, but also improve the adsorption capacity. The adsorption isotherm obeys the Langmuir model, with the saturation adsorption capacity of 2433 mg/g for the composite hydrogel AA-IA-APT5. The as-prepared composite hydrogel shows almost a constant and high adsorption capacity in a wide pH range from 4.0 to 10.0 and, can be regenerated and reused for several times. Furthermore, the composite hydrogel shows high adsorption selectivity for cationic dyes in the case of mixed dyes.

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1. Introduction

Malachite green (MG), a dark-green cationic triarylmethane dye, is highly effective against fungal attacks and protozoan infections and has been extensively used as the biocide in the aquaculture industry. Also, this dye is used as a food coloring agent, food additives, a medical disinfectant and as well as a dye in silk,

leather, and paper industry, etc. However, MG can cause carcinogenesis, mutagenesis, chromosomal fractures, teratogenicity and respiratory toxicity, and the toxicological effects make this dye receive much concern regarding its wide use [1–3]. Due to the environmental persistence and acute toxicity, MG has been banned in aquaculture, but this dye is still used for non-aquaculture purposes and discharged directly into the water body. Therefore, there is a growing recognition that the removal of MG from aqueous effluents is essential to prevent the environmental pollution before they are discharged into the water environment.

* Corresponding author. Tel.: +86 931 4968118; fax: +86 931 8277088.

E-mail address: aqwang@licp.cas.cn (A. Wang).

Various treatments including mainly physical, chemical and biological processes have been developed to remove the dyes from industrial effluent [4,5]. Among all of the methods proposed, the physical adsorption is considered to be the most popular and efficient method due to its high efficiency, simplicity of design and ease of operation. Therefore, a large number of investigations have been performed for the MG removal using various adsorbents, such as activated carbon [6,7], clays [8,9], zeolite [10], chitin [11], agricultural wastes [12,13], and metal–organic frameworks [14], etc. However, the adsorption capacities of most of the reported adsorbents are quite limited. As a consequence, highly effective adsorbent materials are gaining much attention in recent years.

Hydrogels are three-dimensional networks of polymer chains that can swell but cannot dissolve in water. Hydrogels can be formed by physical or chemical crosslinking using different monomers with various functional groups, which can be designed and tailored to target the specific applications encountered. Recently, hydrogels have been used as the adsorbents to efficiently remove many kinds of pollutants from aqueous solutions, such as heavy metals [15,16], dyes [17,18], ammonium ions [19,20] and so on. To reduce the product cost and improve the comprehensive properties including but not limited to adsorption capacity, adsorption rate and gel strength, different inorganic components had been incorporated into the polymeric networks, such as attapulgite [21], sepiolite [22], kaolin [23], montmorillonite [24], vermiculite [25], rectorite [26], halloysite [27], illite/smectite [28], tourmaline [19], hydroxyapatite [29], etc. In addition, some special inorganic component can be utilized to satisfy various situations for water treatment. For example, the incorporation of TiO₂ into the hydrogel can provide the hydrogel with the photocatalytic properties [30] and Fe₃O₄ will afford the hydrogel with the magnetic separation properties [31].

Generally, the hydrogels are obtained with the gel-form, which requires much more energy to dry, to smash and to granulate. Previously, we have obtained the granular hydrogel using ammonium persulfate as the thermal initiator under an inert N₂ atmosphere [32,33]. Here we report a facile preparation of granular hydrogel via radical polymerization at room temperature and atmospheric conditions with Vc/H₂O₂ as the coupling redox agent. The resulting composite hydrogel was then used as the adsorbent to remove MG from aqueous solution. Here, attapulgite (APT), a kind of hydrated octahedral layered magnesium aluminum silicate mineral, was introduced into this hydrogel to improve the comprehensive adsorption properties. This granular hydrogel is constructed with the three-dimensional structured network and abundant carboxylic and carboxylate groups, which can provide potential adsorption sites for strong interaction with MG molecules. The adsorption properties were systematically investigated in single and mixed dye solutions. The adsorption kinetics and adsorption isotherms, as well as the effects of pH, APT content and IA/AA ratio were all studied.

2. Materials and methods

2.1. Materials

Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was purified by vacuum distillation before polymerization. Itaconic acid (IA, Tokyo Chemical Industry Co. Ltd., Japan), chitosan (CTS, with an degree of deacetylation of 90% and average molecular weight of 3.0×10^5 , Zhejiang Yuhuan Ocean Biology Co. Ltd., Zhejiang, China) and *N,N*-methylenebisacrylamide (MBA, chemically pure, Shanghai Yuanfan additives plant, Shanghai, China) were used as received. Ascorbic acid (Vc) and hydrogen peroxide solution (H₂O₂) were analytical grade and

provided respectively by Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China) and Jiangsu Sanmu Group Co. Ltd., (Jiangsu, China). Natural attapulgite (APT, industrial grade, Xuyi R&D Center for Application of Attapulgite Clay, Lanzhou Institute of Chemical Physics, CAS) was milled and sieved through a 200-mesh screen prior to use. Other reagents were all analytical grade and used without further purification.

2.2. Preparation of composite hydrogel

Typically, 0.3 g CTS was dissolved in 45 mL distilled water containing 3.6 g AA, 0.15 g MBA and an appropriate amount of IA in a 250 mL three-neck flask equipped with a mechanical stirrer. After stirring at 500–600 rpm for 30 min at room temperature (12 ± 2 °C), APT powder was dispersed into above mixture for 20 min, followed by adding 50 mg Vc and 5 mL 3% H₂O₂ solution freshly prepared. When the polymerization reaction was carried out for 1 h in atmospheric oxygen at room temperature, the resulting granular products were poured into 4.0 mol/L NaOH solution to equilibrate for 4 h with the final pH value of 6.0–7.0. By then, the swollen hydrogel was dehydrated with industrial alcohol for several times and dried at room temperature prior to use. The as-prepared hydrogel was denoted as AA–IA–APT_x (*x* is the percentage of APT), and the typical digital photographs of granular hydrogels were shown in Fig. S1 (Supporting Information). All hydrogels used for the adsorption experiment had a particle size in the range of 40–80 mesh.

2.3. Determination of swelling degree

Determination of swelling degree of hydrogels was performed through immersion of pre-weighed 20 mg samples in 200 mL distilled water at ambient temperature (12 ± 2 °C) for 6 h until the swelling equilibrium was reached. By then, these hydrogels were separated from the water by filtrating with a 100-mesh stainless screen and hanging up for 10 min. The swelling degree (SD) was gravimetrically determined by the following formula:

$$SD = (m_s - m_d)/m_d \quad (1)$$

where *m_s* and *m_d* were the swollen and dry weight of each hydrogel, respectively.

2.4. Adsorption experiments

In single dye solution: Adsorption experiments were performed in a series of 50 mL conical flasks containing 20 mg adsorbent and 40 mL MG solution. The mixtures were shaken in a thermostatic orbital shaker (THZ-98A) at 30 °C/150 rpm for a given time, and then the adsorbents were filtrated directly with a 100-mesh stainless screen. The equilibrium MG concentration in the supernatant was determined by a TU-1900 double-beam UV–vis spectrometer at the maximum wavelength of 615 nm for MG. The adsorption capacity for MG was calculated according to the following equation:

$$q_e = (C_0 - C_e)V/m \quad (2)$$

where *q_e* is the adsorption capacity in mg/g, *C₀* and *C_e* are the initial and equilibrium concentrations of MG in mg/L, *V* is the volume of MG solution in mL, and *m* is the mass of adsorbent used in mg.

The adsorption kinetics study was performed by varying the contact time from 0 to 300 min at 30 °C/150 rpm and natural pH with an initial MG concentration of 1000 mg/L and adsorbent amount of 20 mg/40 mL. To study the adsorption isotherms, a series of MG solutions with different concentrations from 200 to 1800 mg/L were contacted with 20 mg adsorbent for 5 h at 30 °C/150 rpm and natural pH. The influences of pH on the adsorption

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