Journal of Colloid and Interface Science 516 (2018) 98–109

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

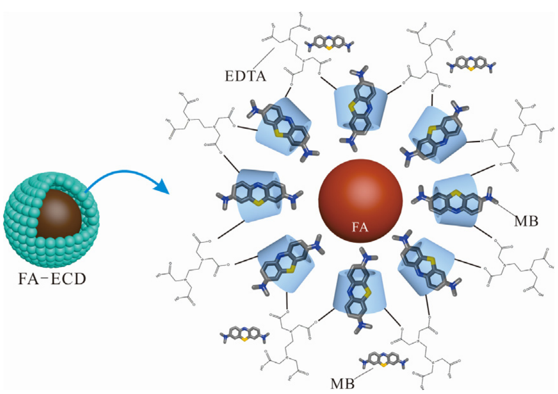
Characterization of EDTA-cross-linked β-cyclodextrin grafted onto Fe-Al hydroxides as an efficient adsorbent for methylene blue

Ningning Liu [a], Yunhai Wu [a,*], Haitao Sha [b]

[a] Key Laboratory of Integrated Regulation and Resources Development of Shallow Lakes, Ministry of Education, Hohai University, Xikang Road #1, Nanjing 210098, China
[b] College of Environment, Hohai University, Xikang Road #1, Nanjing 210098, China

GRAPHICAL ABSTRACT

The selected graph can not only express the preparation of EDTA-cross-linked β-cyclodextrin grafted onto Fe-Al hydroxides, but also revealed the adsorption process of MB, which showed the purposes of this work simultaneously.



ARTICLE INFO

Article history:
Received 31 October 2017
Revised 31 December 2017
Accepted 15 January 2018

Keywords:
Fe-Al
EDTA
β-Cyclodextrin
Methylene blue
Adsorption

ABSTRACT

The synthesis process of Fe-Al hydroxides coated with ethylenediaminetetraacetic acid (EDTA)-cross-linked β-cyclodextrin polymer (FA-ECD) and its utilization in the adsorption of methylene blue (MB) were investigated. The FA-ECD before and after adsorption was characterized by scanning electron microscopy (SEM), Brunauer–Emmet–Teller (BET) analysis, Fourier-transform infrared (FTIR) spectroscopy, thermogravimetric (TG) analysis, and X-ray diffraction (XRD). In addition, the EDTA and β-cyclodextrin contents were determined quantitatively. The optimization of several variables such as contact time, pH, initial concentration, and adsorbent dosage achieved the maximum removal percentages in mild conditions. The results revealed that the adsorption process mainly depended on the pH value and the optimal adsorption capacity of the MB was 60.71 mg/g at pH 8. Subsequently, the experimental equilibrium data at different temperatures were fitted with the Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models; the Freundlich model provided the best results. In addition, the pseudo-second-order kinetic model best described the adsorption of the MB. The thermodynamic analysis proved that the adsorption process was endothermic and spontaneous.

* Corresponding author.
E-mail address: hjywyh@hhu.edu.cn (Y. Wu).

https://doi.org/10.1016/j.jcis.2018.01.056
0021-9797/

Nomenclature

C_e	liquid phase concentration of dye at equilibrium (mg/L)
C_0	initial concentration of dye (mg/L)
C_t	concentration of dye at time of t (mg/L)
M	the weight of the adsorbents used (g)
V	the volume of aqueous solution (L)
q_e	amount of solute adsorbed per unit weight of the adsorbent at equilibrium (mg/g)
q_m	the maximum layer adsorption capacity (mg/g)
K_L	the coefficient of Langmuir isotherm model (L/mg)
K_F	Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg/g)
n	the Freundlich model coefficient
q_t	amount of solute adsorbed per unit weight of the adsorbent at time t (mg/g)
k_1	equilibrium rate constant of pseudo-first-order adsorption (g/mg min)
k_2	equilibrium rate constant of pseudo-second-order adsorption (g/mg min)
k_{ext}	external diffusion constant (min^{-1})
$k_{p,i}$	the intraparticle diffusion rate parameters of different stages (mg/g $min^{0.5}$)
c_{NaOH}	the concentration of used NaOH (mg/L)
c_{HCl}	the concentration of used HCl (mg/L)
V_{NaOH}	the volume of used NaOH (L)
V_{HCl}	the volume of used HCl (L)
m	the weight of sample (g)
C_{ad}	liquid concentrations of reduced metal ion (mg/L)
ΔG^0	Gibbs free energy change
ΔH^0	the enthalpy change (kJ/mol)
ΔS^0	the entropy change (J/(mol K))
η	the adsorptive removal efficiency (%)
R	gas constant (8.314 J/(mol K))
T	absolute temperature (K)
t	time (minute)

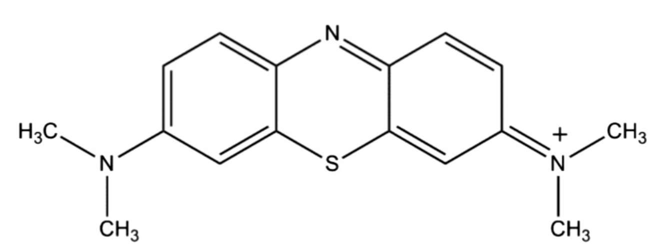
1. Introduction

Dyes are widely used in many rapidly developing industries, including the rubber, paper, cosmetic, textile, and plastic industries and are commonly discharged into the environment without pretreatment [1–3]. The presence of dyes in the aqueous environment is highly visible and aesthetically unpleasant, even at very low concentrations and the intense color can decrease the transmission of sunlight through water and thus lead to the damage of aquatic plants [4,5]. In addition to the effect of color, several kinds of dyes are hazardous to aquatic organisms due to their carcinogenic properties [6–8]. Dyes in an aqueous environment are difficult to degrade by the self-purification of the water body due to their high stability and complex aromatic structures [2]. Thus, the removal of dyes from effluents is a very important issue.

The most commonly employed conventional methods for removing dye from wastewater are ozonation, oxidation, ion exchange, chemical precipitation, membrane separation, adsorption, etc. [9–11]. Among these techniques, adsorption is considered the most promising method due to the simplicity of the design, low cost, and easy operation [12]. Numerous studies have been devoted to searching for suitable adsorbents including MCM-41, SBA-15, activated carbon, zeolite, and diatomite. These adsorbents all have certain drawbacks with regard to cost or performance, thus researchers have attempted to synthesize an efficient and inexpensive adsorbent.

Fe-Al bimetallic hydroxides (FA), which possess a large pore volume, a high surface area, and a regular channel structure, have been prepared by co-precipitation and have been used for the adsorption of heavy metal ions in an aqueous environment in recent years [13]. Due to the functional groups on the surface of the FA and the high surface area, the FA removes the metal ions in solution effectively. However, the FA is not effective for the adsorption of dyes in solution. In the design of an improved FA for a specific substance, surface modification facilitates the adsorption capacity and selectivity. Furthermore, β-cyclodextrin has drawn much attention due to its special physical and chemical properties [14]. β-cyclodextrin is a natural cyclic oligosaccharide decomposed from starch via cyclodextrin saccharin invertase and consists of seven glucose units with many primary hydroxyl groups on the outside shell while the inner cavity contains many secondary hydroxyl groups; as a result, the outer surface of the molecule is strongly hydrophilic and the inner surface has a hydrophobic cavity [15,16]. This special structure allows host molecules to form non-covalent host-guest inclusion interactions, which can occur for a wide range of host molecules with a suitable size and polarity; this enhances the stability and improves the solubility of the guest molecules and is widely applied in the field of material and drug release [17–19]. In the process of using β-cyclodextrin to modify the FA, the crosslinking agent is very important. In earlier studies, epoxy chloropropane (*EPI*) and glutaraldehyde (GLA) were usually used as crosslinking agents. However, the two agents are both reported to have high toxicity and carcinogenicity and they can cause secondary contamination during water treatment [20]. Thus, ethylenediaminetetraacetic acid (EDTA) has attracted increased attention as a crosslinking agent on account of its low toxicity and low cost. In addition, it has been shown that EDTA can be degraded in zero-valent iron/water/air at room temperature [21], indicating that EDTA is an easily degradable and environmentally-friendly crosslinking agent. The polymer adsorption due to the crosslinking process is environmentally friendly and ensures that no secondary pollution occurs during the water treatment.

Thus, this study is focused on researching the application of Fe-Al hydroxides coated with EDTA-cross-linked β-cyclodextrin (FA-ECD) for the removal of dyes (methylene blue (MB)) in an aqueous environment. The main objective of this study is to investigate the adsorption behavior of MB, whose structure is depicted in Scheme 1, by the novel adsorbent FA-ECD. The influences of the adsorbent dosage, time, pH, and initial concentration are also determined. In addition, the adsorbent before and after adsorption is characterized by scanning electron microscopy (SEM), energy



Scheme 1. Structure of MB.