Science of the Total Environment 640–641 (2018) 243–254

Contents lists available at ScienceDirect

Science of the Total Environment

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

Evaluation of a novel dextran-based flocculant on treatment of dye wastewater: Effect of kaolin particles

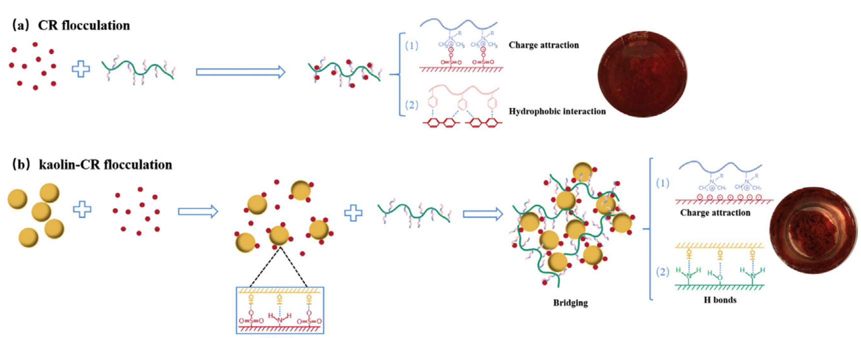
Chuanliang Zhao [a,b], Huaili Zheng [a,b,*], Yongjun Sun [c], Shixin Zhang [a,b], Jianjun Liang [a,b], Yongzhi Liu [a,b], Yanyan An [a,b]

[a] *State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, Chongqing 400044, China*
[b] *Key Laboratory of the Three Gorges Reservoir Region's Eco-Environment, State Ministry of Education, Chongqing University, Chongqing 400045, China*
[c] *Jiangsu Key Laboratory of Industrial Water-Conservation & Emission Reduction, College of Environment, Nanjing Tech University, Nanjing 211800, China*

HIGHLIGHTS

- A dextran-based flocculant DAB was designed and prepared by ultrasound initiated polymerization technique.
- Flocculation of dye wastewater was studied.
- The high flocculation performance of DAB is due to structural advantages.
- The existence of suspended solids markedly improved the removal of dyes.
- Zeta potentials, FTIR and XPS spectra of flocs were measured for mechanism study.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 February 2018
Received in revised form 23 May 2018
Accepted 23 May 2018
Available online xxxx

Editor: Zhen (Jason) He

Keywords:
Dextran-based flocculant
Surface-active monomer
Ultrasound
Congo red
Kaolin
Flocculation mechanism

ABSTRACT

Graft modified flocculants have recently received increasing attention in the field of water treatment as they have the combinative advantages of synthetic and natural polymeric flocculants. In this work, surface-active monomer benzyl(methacryloyloxyethyl)dimethylammonium chloride (BMDAC) was selected to graft on dextran (DX) with high molecular weight (10.3×10^6 g/mol) produced through enzyme-catalyzed process in order to remove dissolved dyes from wastewater. The flocculant (DAB) was fabricated by ultrasound initiated polymerization technique, and the structure characterization of FTIR, $^1H/^{12}C$ NMR, XRD and XPS spectrum confirmed the successful grafting. Then the Congo red (CR) removal efficiency by DAB was optimized based on the flocculation conditions, including wastewater initial pH, flocculant dosage and initial dye concentration. The effect of suspended solids on the removal of dyes was evaluated in kaolin-CR simulated wastewater. The results indicated that the optimal removal efficiency of CR was 68.1% and 88.2% in single CR and kaolin-CR flocculation system, respectively. The improvement of removal efficiency was attributed to the fact that partial CR molecules were adsorbed onto kaolin particles before flocculation, and were synergistically flocculated accompanied by kaolin particles. Finally, the flocculation mechanism was discussed by a detailed investigation of the zeta potentials, FTIR and XPS spectra of flocs, which can provide important reference for optimizing the flocculation conditions and designing novel high-performance flocculants.

1. Introduction

Organic dyes from industries such as textile, rubber, paper, plastics, cosmetics, paints, etc., will inevitably be discharged into wastewater

* Corresponding author at: State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, Chongqing 400044, China.
E-mail address: zhl6512@126.com (H. Zheng).

https://doi.org/10.1016/j.scitotenv.2018.05.286
0048-9697/© 2018 Published by Elsevier B.V.

(Vahidhabanu et al., 2017). It is estimated that more than 7×10^5 tons/year dyes are produced all over the word which are characterized as toxic, non-biodegradable, carcinogenic and mutagenic for creatures. Therefore, inappropriate treatment of large amount of wastewater containing dyes will cause serious environmental problems. In addition, many dyes are visible in water at concentrations as low as 1 ppm, which is enough to present an aesthetic problem (Subramonian and Wu, 2014; Low et al., 2012). Generally, dyes can hardly be removed by means of conventional wastewater treatment such as activated sludge and anaerobic digestion due to its complex, aromatic molecular structure and stable azo linkage (Vimonses et al., 2009). Congo red (CR) is a kind of typical benzidine-based anionic azo dye, which is widely used in various domains (Shu et al., 2015a). Over the past decades, a large number of techniques for dyes removal from wastewater have been reported. However, most of the research focused on the removal of a single dye, and ignored the coexisting suspended solids in industrial wastewater (Liu et al., 2017; Mohanta et al., 2013; Rong et al., 2015). It remained unclear that whether suspended solids will influence the removal of dyes. Therefore, it is necessary to elucidate the effect of suspended solids on CR removal.

Among various water treatment techniques, coagulation/flocculation display unique advantages in dyes wastewater treatment because of easy operation, low cost, and satisfying treatment efficiency (Teh et al., 2016; Yang et al., 2013). As coagulants/flocculants are the crucial factors in determining coagulation/flocculation performance, the screening and design of highly efficient and cost-effective flocculants become a research emphasis. Traditional metal coagulants have gradually faded out of view because of its high sludge production, sensitivity to pH and limited application. In recent years, many research reported that polymeric flocculants, synthetic as well as natural, showed excellent flocculation performance. However, non-biodegradability and biological toxicity of synthetic polymeric flocculants derived from petroleum-based and non-renewable raw materials have restricted their development, while natural flocculants are confronted with problems of short shelf life and active groups easy to biodegrade with time (Lee et al., 2014; Liu et al., 2018). The disadvantages of natural flocculants could be overcome by modifying the natural polymers via grafting, oxidation, depolymerisation, substitution or cross linking to form anionic, cationic, and non-ionic polymers for treatment of wastewater (Shak and Wu, 2016). Therefore, extensive attention has been given to graft modified flocculants which have the combinative advantages of synthetic and natural polymeric flocculants.

Dextran (DX), a natural polysaccharide, consists of glucose monomers linked predominantly by α-D-(1–6) in the main chain and a variable amount of α-D-(1–2), α-D-(1–3) and α-D-(1–4) in branches, which is mainly produced by fermentation method at the industrial level (Tingirikari et al., 2014). With the superiority of a wide variety of molecular weights and lower likelihood to degrade under mild acid and basic conditions, DX has emerged as an ideal candidate for graft modification in the water treatment field. The ceric ammonium nitrate (CAN) was extensively used to generate free radical sites on the DX backbone, where the graft chains of monomers, such as sodium acrylate and acrylamide (AM), were introduced (Krishnamoorthi et al., 2010; Krishnamoorthi et al., 2007; Li et al., 2016). These copolymers were effective in flocculating suspended particle wastewater, but few literatures about the removal of dyes. There are two main reasons, one is that dyes exist in water in the form of dissolved molecules or ions, which are difficult to be flocculated into bigger aggregates. To remove these small-sized contaminants, flocculants should possess high molecular weight (HMW). Nowadays, the molecular weight of DX produced by enzyme-catalyzed process can achieve 10^9 Da, which is higher than that by traditional fermentation method, meeting the requirement of HMW flocculants (Faucard et al., 2018). The other reason is that electrostatic repulsion interactions between dye molecules make the system difficult to destabilize. Considering that CR is electronegative, cationic monomers should be grafted onto DX backbone to neutralize negative charges. In our previous study, surface-active monomer benzyl (methacryloyloxyethyl)dimethylammonium chloride (BMDAC) presented outstanding performance: on the one hand, quaternary ammonium groups can provide cationic characteristics; on the other hand, hydrophobic benzyl groups can enhance the interaction with contaminants (Zhao et al., 2017; Zhao et al., 2018). Nevertheless, considering the high price of BMDAC, AM and BMDAC were simultaneously chosen as graft monomers in order to synthesize highly efficient and cost-effective flocculants.

Graft copolymerization in aqueous solution can be initiated by heat, high energy radiation (gamma rays or electron beam), ultraviolet, etc. (Da Silva et al., 2007; Li et al., 2017c; Vahdat et al., 2007; Wang et al., 2008). Among all the initiation methods, thermal initiation has the longest reaction time of about 12-24 h, indicating the lowest reaction efficiency. Furthermore, the inappropriate heating may cause cross-linking of copolymer, thereby reducing dissolubility. High energy radiation is a better method of generating free radicals but this method can result in radiolysis of polysaccharide main chains. The application of photochemical initiation by UV-light is also limited because the low penetration ability of UV-light is just suitable for surface grafting. In recent years, ultrasonic initiation achieved varied success due to the characteristics of faster polymerization rate, narrower molecular weight distribution and higher monomer conversion (Cravotto and Cintas, 2006). The ultrasound initiated polymerization technique is regarded as simple, effective, economical and environment friendly, which make it potential for the commercial process of DAB. More importantly, the function of surface modification may improve the surface roughness of products, which is propitious to DAB hydration and dissolution during flocculation of dye wastewater. To the best of our knowledge, the investigation of ultrasound initiated AM and BMDAC grafted dextran for dye wastewater treatment has not yet been available to date.

In view of all the aforementioned aspects, a biopolymer-based flocculant (dextran-*graft*-poly(AM-BMDAC), DAB) was synthesized using ultrasound initiation method. The structure of the obtained polymer was analyzed by FTIR, ^{1}H NMR, ^{12}C NMR, XRD, XPS spectroscopy. Then the CR removal efficiency was optimized based on the flocculation conditions, including wastewater initial pH, DAB dosage and initial CR concentration. The effect of suspended solids on the removal of dyes was evaluated in kaolin-CR simulated wastewater as a comparison with single CR flocculation. Finally, the flocculation mechanism was discussed by a detailed investigation of the zeta potentials, FTIR and XPS spectra analysis of flocs.

2. Materials and methods

2.1. Materials

AM and BMDAC used in this experiment were all of technical grade and used without further purification. The monomer AM (98.5%, w/w) was obtained from Jiangxi Changjiu Biochemical Industry Co., Ltd. (Nanchang, China); BMDAC (60 wt% in water) was procured from Zibo Wonderful Chemical Co., Ltd. (Zibo, China). Dextransucrase was extracted from an engineered strain *E. coli* BL21 (DE3)/pET28-dexYG (Zhang et al., 2008). Potassium persulfate ($K_2S_2O_8$) were purchased from Aladdin Co. Ltd. (Shanghai, China). The used kaolin (average particle diameter: 4.18 μm) and CR were all of chemical grade and purchased from Chengdu Kelong Chemical Reagent Co. Ltd. (Chengdu, China). All aqueous and standard solutions were prepared with distilled water.

2.2. Preparation of DAB

HMW dextran was synthesized through dextransucrase-catalyzed process, and the detailed synthetic procedure was given in Supplementary Text S1. As depicted in Scheme 1, DAB was prepared through ultrasound initiation taking AM and BMDAC as grafting monomers and $K_2S_2O_8$ as initiator. The purpose of ultrasound was to induce acoustic