Journal of Environmental Management 218 (2018) 31–38

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Removal of the commercial pesticides Novadim Progress, Bordeaux mixture and Karate Zeon by pullulan derivatives based flocculants

Luminita Ghimici*, Marieta Constantin

"Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda, 41A, 700487 Iasi, Romania

ARTICLE INFO

Article history:
Received 31 January 2018
Received in revised form
23 March 2018
Accepted 11 April 2018

Keywords:
Pullulan derivatives
Pesticides
Flocculation mechanism
UV–Vis spectroscopy
Zeta potential

ABSTRACT

Cationic pullulan derivatives have been synthesized and evaluated, for the first time, as flocculants for the separation of the commercial pesticides, Novadim Progress (organophosphoric type), Bordeax mixture and Karate Zeon (pyrethroid type) from synthetic wastewater. The investigated polymer samples contained either pendent tertiary amine or quaternary ammonium salts groups. The separation efficiency was followed by UV–Vis spectroscopy, while the information regarding the mechanism involved in the separation of pesticide particles have been obtained by zeta potential. UV–Vis spectroscopy data showed strong pesticide particles/polycation interactions in case of Novadim Progress and Bordeaux mixture (maximum pesticide removal between 90% and 98%). Good separation efficiency (around 80%) of Karate Zeon emulsion was also noticed. The zeta potential measurements indicated that the charge neutralization was the common flocculation mechanism for the removal of these pesticides. In addition, the hydrogen bondings and chelation of copper ions by amide and/or tertiary amino groups of the polycations had a noteworthy contribution to the pesticide removal.

1. Introduction

The production of different classes of pesticides has been increasingly throughout the time because of the extensive use in agriculture field in order to control various pests that threaten the health of growing crops. Unfortunately, at the same time with improving the crop yields and health, the pesticides take along adverse side effects for the environment and human life (Kouras et al., 1998; Doulia et al., 2016). Traces of these contaminants may be found in the wastewaters from pesticide production plants, soil and surface water and can also remain on food (fruits and vegetables) being a major concern for many consumers. In order to reduce and eliminate the content of pesticides, the scientific community developed different methods involving nanofiltration, adsorption, chemical oxidation, electrochemical techniques (electro-oxidation, electro-coagulation and electro-Fenton), photocatalytic and biological degradation etc (Rani et al., 2017; Garcia-Segura et al., 2017; Muñoz et al., 2017; Rawtani et al., 2018). The pesticides removal from wastewaters by means of coagulation and flocculation methods is less investigated (Latkowska and Figa, 2007; Misra et al., 2013). The above mentioned methods, performed either by means of inorganic additives (aluminum sulfate and ferric chloride) or polymers (synthetic and natural) (Bolto and Gregory, 2007), proved to be the most successful primary wastewater treatment techniques because they are cheaper and easy of operate, as compared to other processes. Lately, biopolymers are preferred due to the advantages of being inexpensive, biodegradable and non-toxic (Rao et al., 2014; Singh et al., 2000). However, in the flocculation process the polysaccharides biodegradability can lead to the loss of flocs stability and strength (Singh et al., 2000). Moreover, some of polysaccharides characteristics could limit their application for certain purposes in biology, medicine, cosmetics, food, textile, papermaking etc. industries. For these reasons, much attention has been paid to modify them by physical, biological and chemical methods (Li et al., 2016). Cumpstey (2013) covered in his review some of the chemical methods, such as ester and ether formation using saccharide oxygen nucleophiles; the insertion of heteroatomic nucleophiles into polysaccharide chains; the oxidation of polysaccharides, including oxidative glycol cleavage, chemical oxidation of primary alcohols to carboxylic acids and enzymatic oxidation of primary alcohols to aldehydes; nucleophilic reactions of the amines of chitosan. Both ionic and nonionic derivatives of different polysaccharides (guar gum, cellulose, starch, konjac glucomannan, dextran, pullulan) with better properties have been

* Corresponding author.
E-mail address: lghimici@icmpp.ro (L. Ghimici).

https://doi.org/10.1016/j.jenvman.2018.04.056
0301-4797/

obtained (Li et al., 2016; Prado and Matulewicz, 2014; Liu et al., 2015). Lot of them were tested and showed good results in removal of both inorganic and organic contaminants from wastewaters (Prado and Matulewicz, 2014; Tian et al., 2010; Ghimici and Constantin, 2011; Ghimici and Nichifor, 2012; Zhang et al., 2013; Liimatainen et al., 2014; Kyzas and Bikiaris, 2015; Ghimici and Suflet, 2015; Yang et al., 2016; Pestov and Bratskaya, 2016; Ren et al., 2016; Kanmani et al., 2017; Salehizadeh et al., 2017; Grenda et al., 2017). Few studies have demonstrated that some cationic polysaccharides in solution can decrease the concentration of some commercial pesticides from synthetic wastewaters: Fastac 10EC (Ghimici and Nichifor, 2015; Ghimici and Constantin, 2015), Decis, Dithane (Ghimici et al., 2016). Thus, cationic dextran and pullulan derivatives (D40-EtX and DMAPA$_x$-P, respectively) as well as chitosan based flocculants with different charge content have shown high removal efficiency (around 90%), for the pesticide formulations mentioned above; they contain α-Cypermethrin (Fastac 10 EC), Deltamethrin (Decis) and Mancozeb (Dithane) as active ingredients. The efficiency exhibited by the cationic pullulan derivatives with pendent tertiary amine groups (DMAPA$_X$-P) in separation of Fastac 10 EC from model emulsion (Ghimici and Constantin, 2015) stimulated us to evaluate them in removal of other pesticides belonging to different classes, Novadim Progress - organophosphorus type with Dimethoate as active ingredient, Karate Zeon - pyrethroid type, with lambda- Cyhalothrin as active ingredient, and fungicide Bordeaux mixture. The results were compared with those obtained when some new pullulan derivatives containing quaternary ammonium salt groups (DMEAPA-P and DMBzAPA-P) were used as flocculants. To our knowledge such a study has not been undertaken previously.

The separation efficiency was followed by UV–Vis spectroscopy while information regarding the mechanism involved in the separation of pesticide particles have been obtained by zeta potential measurements.

2. Experimental

2.1. Materials

2.1.1. Materials for synthesis of flocculant

Pullulan (P) (Mw = 200 kg mol^{-1}) was purchased from Hayashibara Lab. Ltd. (Okoyama, Japan). 3-dimethylamino-1-propylamine (DMAPA), ethyl iodide (EI), benzyl chloride (BzCl), N,N′-carbonyldiimidazole (CDI), 4-(Dimethylamino)pyridine (DMAP) were purchased from Fluka (Buchs, Switzerland) and have been used as received. Dimetylsulfoxide (DMSO) and dimethylformamide (DMF) were obtained from Fluka and distilled under vacuum prior the use.

2.1.2. Pesticides

Novadim Progress (Cheminova A/S, Denmark) (labeled in the paper *NP*) is commercially available in small bottles/vials: 20 mL solution (Dimethoate- 400 g L^{-1}; solvent cyclohexanone, xylene) (chemical structure in Fig. 1a).

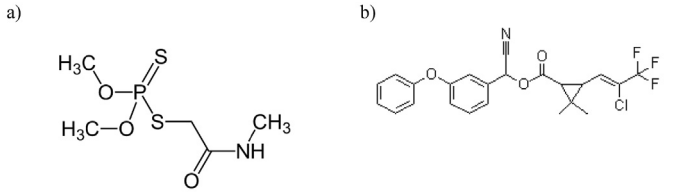

Fig. 1. Chemical structure of pesticides: Dimethoate (a), lambda- Cyhalothrin (b).

Karate Zeon (Syngenta Limited, England) (labeled in the paper *KZ*) is commercially available in small bottles/vials: 2 mL solution (lambda-Cyhalothrin: 50 g L^{-1}; solvent naphtha (petroleum), heavy arom., 1,2 benzisothiazolin-3one) (chemical structure in Fig. 1b).

Bordeaux mixture MIF type (IQV, Spain) (labeled in the paper *BM*) is commercially available in packs of 50 g (20% copper sulfate).

2.2. Methods

2.2.1. Synthesis of pullulan derivatives

2.2.1.1. Dimethylamino-propylamine pullulan (DMAPA$_x$-P). Three samples with pendent tertiary amine groups (Fig. 2) were synthesized by chemical modification of pullulan with a molar mass of Mw = 200 kg mol^{-1} using a procedure previously described by Constantin et al. (2015). Shortly, the polysaccharide was dissolved in DMSO and the hydroxyl groups were activated for 2 h at room temperature by adding a certain amount of N,N′-carbonyldiimidazole. Then, an excess amount of DMAPA (4 mol/mol glucosidic unit of pullulan) was added and the reaction continued for 48 h at room temperature in the presence of DMAP as catalyst. The polymer was recovered by precipitation with acetone, solubilized in water and purified by sequential dialysis against 0.1N HCl, 0.1N NaOH and water. Finally, the polymer was recuperated as a white powder by freeze-drying.

2.2.1.2. Dimethylethylammonium-propylamine pullulan (DMEAPA-P) and dimethylbenzylammonium-propylamine pullulan (DMBzAPA-P). Two samples of quaternary ammonium pullulan were synthesized by the quaternization reaction of DMAPA$_{0.4}$-P (see chemical structure in Fig. 2). Briefly, DMAPA-P polymer (1 g, 1.936 mmol tertiary groups content) was dissolved in 20 mL of DMF. First, for DMEAPA-P synthesis, an appropriate volume of EI (EI/DMAPA molar ratio = 3) in 5 ml of DMF was dropwise added to this solution at 20 °C for 15 min. Second, for DMBzAPA-P synthesis, BzCl (BzCl/DMAPA molar ratio = 1.2) in 10 mL of DMSO was used. Then, the reactions were continued at 50 °C for 24 h. The obtained compounds were precipitated in acetone. The crude product DMEAPA-P was dissolved in 15% (w/v) NaCl solution in order to replace the iodide ions with chloride ions followed by dialysis with deionized water for 3 days to remove inorganic materials and then freeze-dried. The DMBzAPA-P precipitate in acetone was further solved in distilled water and washed by dialysis against distilled water until free of chloride ions. The white powders obtained were stored in vacuum desiccators over P_2O_5 for further analysis.

The polymers code is DMAPA$_x$-P, where P means pullulan, DMAPA is aminopropyl dimethylamine group and x = DS, the degree of substitution of hydroxyl groups with amino groups (number of amino groups per anhydroglucose unit in pullulan). The content in amino groups (DS) was determined by ^{1}H NMR spectroscopy (Constantin et al., 2015). The degree of quaternization was also determined by comparing the peaks integrals assigned to the different amino substituents in the ^{1}H NMR spectrum, before and after quaternization.

2.2.2. Flocculation procedure

The aqueous polycation stock solutions, stabilized at room temperature for 1 day before use, and pesticide emulsion/suspension were prepared in distilled water. The concentration of polymer in its stock solution was 1g L^{-1}, while those of the pesticide model wastewater were: *NP* emulsion: c (%,v/v) = 0.7; *BM* suspension: c (%,w/w) = 0.05; *KZ* emulsion: c (%,v/v) = 0.02. Stable emulsions/suspension of pesticides (sample volume of 500 ml) were obtained by sonication for 15 min using an ultrasonicator VCX 750 SONICS, USA. The zeta potential measurements performed on the synthetic wastewater thus prepared, in the absence of polycations, were: