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The separation of the pyrethroid insecticide Fastac 10 EC by cationic pullulan derivatives

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ABSTRACT

Pullulan derivatives with different content of tertiary amine groups have been evaluated, as flocculants, for the separation of pesticide Fastac 10 EC from model emulsions. The flocculation performance of the cationic polysaccharide samples at different conditions (Polycation dose, pH and pesticide concentration) was followed by UV–vis spectroscopy measurements. The results show similar values for the maximum removal efficiency (around 90%), irrespective of the ionic groups content and an increase (from 80% to more than 90%) with initial pesticide concentration increase (from 0.02% to 0.04%). The optimum polycation dose decreased with increasing substitution degree and decreasing the emulsion pH. The supernatant zeta potential dependence on the cationic polysaccharide dose indicated a charge neutralization mechanism for the flocculation of pesticide particles, that was supported by particle aggregates size measurements.

1. Introduction

The extensive use of pesticides in the agriculture field has led, in a great measure, to the crops production improvement due to efficiency of these chemicals in controlling harmful pests [1]. Unfortunately, along with this benefit, pesticides have some undesirable properties, such as resistance to microbial degradation and ability of accumulation in the environment [2], which can cause the contamination of soil and surface waters, hence major environmental problems. An important quantity of pesticide is also found in the wastewaters that come from pesticide production plants. The concern regarding the pesticides arises from their toxicity and carcinogenic effect on the living organisms [3]. Therefore, many scientists focused their investigations toward finding methods for pesticides removal from soil as well as surface and industrial wastewaters. These include adsorption on activated carbon [4–6], different clays (kaolin, montmorillonite, bentonite) [7], organo-zeolites [8], hypercrosslinked polymers [9], electrochemical and advanced oxidation techniques [10–12], nanofiltration [13–15] or combined methods [16,17]. However, many of these technologies have limitations because they either are too expensive or not ecofriendly. On the contrary, coagulation/flocculation processes with inorganic additives (aluminum sulfate and ferric chloride) as well as with macromolecular compounds (nonionic or ionic) are cheaper, environment friendly (especially when natural polymers are used) and easy of operate, as compared to other processes. These methods have been successfully applied in removing clays, metal oxides, dyes, oil etc. [18–23]. The concentration of some pesticides in water was also reduced by inorganic coagulants, namely aluminum- or iron based salts [24,25]. Few data are reported regarding the application of polyelectrolyte solutions for the pesticides wastewaters treatment. For example, some combinations of inorganic salts with the polyelectrolyte Magnafloc and an anionic one (N71605) have been used by Misra et al. [2] and Latkowska and Figa, respectively [26]. In the former case, the Alum: Magnafloc dose of 300:0.25 mg/L was found to be the best one in the coagulation/flocculation process of some agrochemical/pesticide wastewaters with COD reduction of 55.76%; in the latter case, the best pesticide (cyanide) removal results ranged between 45 and 53% using mineral coagulant dose ($FeCl_3$, $Fe_2(S0_4)_3$) of 50 and 100 mg/L and polyanion dose of 1 mg/L. Also, polycation (4-vinylpyridine-co-styrene) (PVP-co-S)–clay (montmorillonite) composites and silver-complexed chitosan microparticles were used as sorbents for the removal of atrazine [27] and methyl parathion [28], respectively. Inspection of the literature data on the pesticides removal does not indicate the using of polyelectrolytes based on pullulan, as flocculants. Pullulan (P) is a biocompatible and biodegradable polymer, which is degraded into non-toxic oligomers or monomers [29]. Its derivatives (nonionic as well as ionic) have extensively used as a coating and packaging material, sizing agent for paper or starch replacer in low-calorie food formulations, cosmetic emulsions and other biomedical applications [30–32]. Therefore, the present study has been directed toward evaluation of the separation properties (by flocculation and sedimentation processes) of novel cationic pullulan derivatives with pendent tertiary amine groups, $DMAPA_X$-P, in a Fastac 10 EC model emulsion. Our previously published results indicated some pullulan derivatives containing various amount and length of grafted cationic chains, poly[(3-acrylamidopropyl)-trimethylammonium chloride], onto polysaccharide backbone as efficient flocculants in aqueous clay suspensions [33].

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