

Cationic Polyelectrolytes Application for Removal of the Novadim Progress and Decis Pesticide Formulations from Synthetic Emulsions

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1. Abstract

The separation efficacy of some synthetic cationic polyelectrolytes and chitosan for removal of the organophosphoric (*Novadim Progress*) and pyrethroid (*Decis*) pesticide formulations from model emulsions has been assessed. The synthetic cationic polyelectrolytes contain the same amount of N,N - dimethyl - 2 - hydroxypropylammonium chloride groups located along the main chain (80%), but different branching degrees. Chitosan samples with viscosity average molecular weight (M_v) between 189-600 kg mol⁻¹ have been used in order to clarify the impact of the molecular mass on the pesticides removal efficacy. UV-Vis spectroscopy measurements show good removal efficiency for *Novadim Progress* (between 92% and 97%) and around 90% for *Decis*. The residual content of pesticides has not been influenced by the molecular mass of CS. Zeta potential data have contributed to the establishment of the main flocculation mechanism (charge neutralization) which governs the pesticides removal.

3. Introduction

Novadim Progress is an organophosphorus type pesticide formulation (insecticide and acaricide) with systemic action whose main active ingredient is Dimethoate ([O,O-Dimethyl S-(N-methylcarbamoylmethyl) phosphorodithioate]) [1]. The agricultural field uses this pesticide to protect, and hence to improve the production of many crops, such as grain, vegetables, fruits, and ornamentals but it is also applied in urban areas [2,3]. Unfortunately, like almost all pesticides, along with the crops production increase, environmental and health problems could arise because of its damage on the living organisms; thus, excessive application of Dimethoate could lead to accumulation in the human body through the food chain, which could disrupt cholinesterase enzyme and cause cholinergic dysfunction or even death [4]. Therefore, several researchers have focused their investigations towards removal of Dimethoate by using different methods, such as photocatalytic degradation using LbL fabricated TiO₂/polymer hybrid films [5], solar photocatalysis employing titanium dioxide [6], biodegradation by bacteria [7], adsorption on gold nanospheres and nanorods [3]. Although, in some cases total elimination of Dimethoate can be achieved, these methods have also drawbacks (the formation of toxic by-products, the complete mineralization of organic matter usually requires long periods of treatment) that could make them unattractive from the economical or technical point of view [6,7]. On the other hand,

the coagulation and flocculation methods are recognized as cheaper and easy to operate processes, as compared to other ones. In spite of that, seldom researches have focused on the application of these methods in purification of the pesticides-containing wastewater [8-11]. The use of aluminum- and iron-based salts or mineral coagulant/anionic polyelectrolyte combinations led to pesticides reduction only up to around 50% [8,10]. However, in recent years, some cationic polyelectrolytes based on polysaccharides (dextran, pullulan, chitosan) have been applied with good results (removal efficiency more than 90%) for pesticide formulations of different type, namely pyrethroids (*Fastac 10EC*- α -Cypermethrin as active ingredient and *Decis* -Deltamethrin as active ingredient), dithiocarbamate (*Dithane M45*- Mancozeb as active ingredient) and Bordeaux mixture [12-16]. UV-Vis spectroscopy data also showed a high decrease of *Novadim Progress* content (around 90%) from synthetic emulsion when cationic derivatives of pullulan [17] and chitosan [18] were used as flocculants. This result was possible because *Novadim Progress* particles are negatively charged (zeta potential for the initial emulsion, $\zeta = -35.3$ mV) due to hydrolysis of some of Dimethoate molecule at the amide groups [19]. Thus, the polyelectrolytes with positive charges in the chain could be more suitable for its removal from wastewater. One has to mention here that besides the charge type (positive or negative), the flocculation process by ionic polymers is also influenced by other parameters such as the chain charge content, the branching degree, the chain

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hydrophobicity, the molecular mass (M), etc. In the previous papers, the influence of charge content of the pullulan derivatives [17] and type of functional groups, amine and thymine groups in chitosan and its derivative, respectively [18] on the Novadim Progress separation efficiency has been, mainly, followed. The high removal efficiency exhibited by the cationic polysaccharide derivatives mentioned above, which contain tertiary amine groups in the chain, prompted us to test some strong cationic polyelectrolytes which bear quaternary ammonium salt groups located in the main chain for the separation of this pesticide. We refer below to synthetic cationic polyelectrolytes with (N,N - dimethyl - 2 - hydroxypropyl) ammonium chloride groups located along the main chain, with different branching degrees (PCA_{20} , PCT_{20}). In addition, a series of chitosan (CS) samples with viscosity average molecular weight (M_v) between 189-600 kg mol^{-1} have been tested in order to clarify the impact of the molecular mass on the pesticides removal efficacy. Quite often, for enhancing its activity, *Novadim Progress* is applied together with pyrethroid pesticides. Therefore, the flocculation efficiency of these polyelectrolytes for removal of *Decis* pesticide formulation has been also evaluated. So far, there is no report regarding the application of polycations PCA_{20} and PCT_{20} in removal of any type of pesticides, while chitosan only with viscosity average molecular weight (M_v) of about 189 kg mol^{-1} has been tested for the reduction of *Novadim Progress* and *Decis* content from model emulsions [18].

4. Materials and methods

4.1. Ionic Polymers

4.1.1. Synthetic Polyelectrolytes: Polyelectrolytes with quaternary ammonium salt (N,N - dimethyl - 2 - hydroxypropyl) ammonium chloride groups located along the main chain were synthesized by condensation polymerization of epichlorohydrin (ECH) with dimethylamine (DMA) and two kinds of polyfunctional amines, namely N,N-dimethyl-1,3-diaminopropane polymer PCA_{20} [20] (chemical structure in Figure 1a) and triethylenetetramine - polymer PCT_{20} (chemical structure in Figure 1b) [21]. The definitions of the abbreviations of these polycations are the followings: PC - polycation; A, T - polyfunctional amine. The number means mole percent of the polyfunctional amine.

The synthetic polyelectrolytes were purified by ultrafiltration (Hollow-Fiber Concentrator CH2A Amicon) and solids were obtained by vacuum freeze-drying (Beta 1-16, Christ, Germany). Polycations were characterized by the content in ionic chlorine (determined by potentiometric titration with 0.02 N aqueous AgNO_3 solution) (Cl_i) and total chlorine (determined by the combustion method - Schöniger technique) (Cl_t): Cl_i 22.92%, Cl_t 23.22%, for PCA_{20} ; Cl_i 23.84%, Cl_t 23.83 for PCT_{20} .

4.1.2. Chitosan: Chitosan Samples (CS) (Figure 2) (Sigma-Aldrich, Germany) were used as received. Their degree of deacetylation of 85% and viscosity average molecular weights between 189 and 600

kg mol^{-1} were determined as previously reported by Kasaii (2010) and Humelnicu et al. 2020 [22,23].

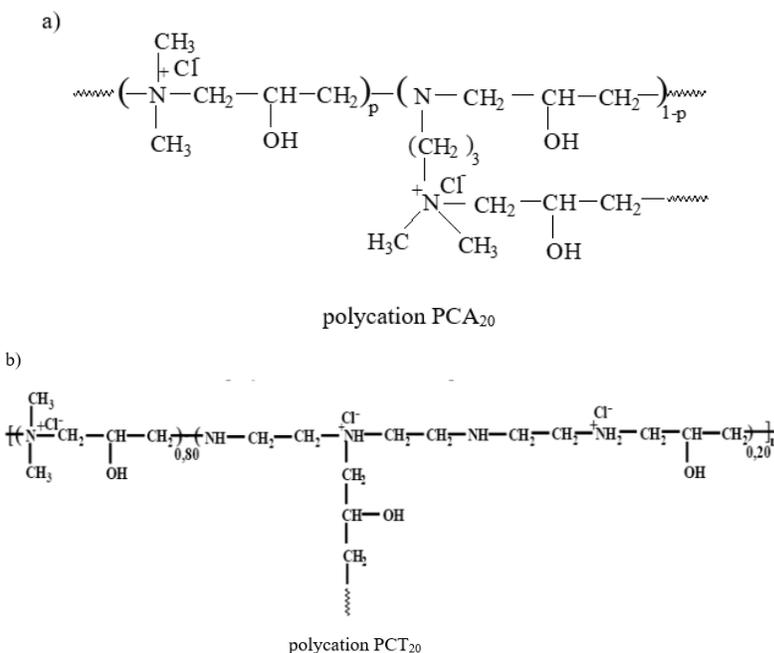


Figure 1. The chemical structure of polyelectrolytes PCA_{20} (a), PCT_{20} (b)

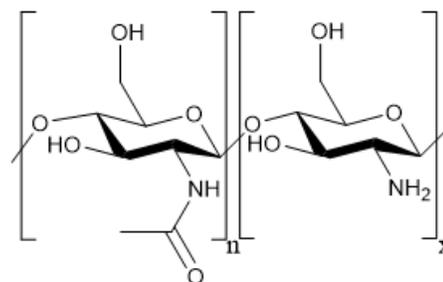


Figure 2. Chemical structure of CS

4.2. 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 Figure 3a).

Decis (Bayer CropScience) (labeled in the paper Dc) is commercially available, in vials with 2 mL solution (Deltamethrin: 50 g L^{-1} ; solvent naphtha (petroleum), heavy arom.) (chemical structure in (Figure 3b)).

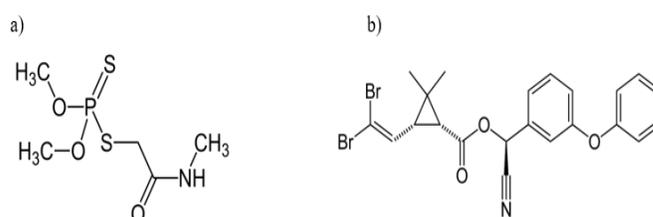


Figure 3. Chemical structure of pesticides: Dimethoate (a), Deltamethrin (b)

4.3. Flocculation Procedure

The polyelectrolyte solutions prepared within one day before the flocculation experiments, either in highly purified deionized water from a Milli-Q PF (Millipore, Switzerland) (synthetic polyelectrolytes) or in acetic acid 1% (v/v) (chitosan) have a concentration of 1 g L^{-1} . Pesticides emulsions with concentrations c (% (v/v)) = 0.7 for *NP* (the initial pH = 5.5) and 0.04 for *Dc* (the initial pH = 4.5) were also prepared with highly purified deionized water. The flocculation experiments were performed at room temperature, using a Cole Parmer stirrer/hotplate with 9 places, according to the method already described [12]. Different volumes of polycation solution were added under stirring (500 rpm) to 50 ml of pesticides synthetic emulsion placed into 100 ml beakers. Stirring was continued with the same speed for about 3 min, and then it was reduced to about 200 rpm for 15 min. After the optimum settling times fixed for each particle (120 min for *NP* and 1200 min for *Dc*) (the period of time after which the pollutants residual absorbance (%) remained almost constant), absorbance measurements (spectrophotometer SPECOL 1300 Analytik Jena) at $\lambda = 601 \text{ nm}$ for *NP* and (267 nm for *Dc*) and zeta potential ones (Zetasizer Nano-ZS, ZEN-3500 model, Malvern Instruments, Malvern, England) were performed on supernatant samples.

The pesticide removal was expressed as percent of the initial absorbance recorded for the pesticide particle emulsions, at time zero (without polymer):

$$\text{residual pesticide absorbance (\%)} = 100 A_f/A_i$$

where, A_i = the absorbance of the pesticide emulsion in the absence of polyelectrolyte and A_f = the absorbance of supernatant after addition of polyelectrolyte.

Triplicate experiments were made and the mean values were calculated. Standard deviation determined for the experiments was $\pm 4\%$.

5. Results and Discussion

5.1. Synthetic Polyelectrolytes

5.1.1. Removal of *NP* Pesticide Formulation: The separation of *NP* particles in the presence of PCA_{20} and PCT_{20} is shown in (Figure 4a). One observes that the addition of polyelectrolytes results in the significant increase of the separation efficiency (up to 85–88%) with the enhancement of polymer dose (up to around 6 mg L^{-1}), followed by an interval (*FW*) between 6 mg L^{-1} to 10 mg L^{-1} for PCA_{20} and between 6 mg L^{-1} and 16 mg L^{-1} for PCT_{20} where removal efficacy higher than 90% has been noticed. *FW* refers to the interval of the polycation dose corresponding to the minimum of the residual contaminants/maximum removal efficacy.

This result could be explained taking into account the type of interaction forces (electrostatic and/or hydrophobic attractions, hydrogen bonding, ion binding) which could come into play be-

tween the polycations and pesticide particles. Both cationic polymers are characterized by a high content of cationic groups on the main chain (80%), while zeta potential for the initial emulsion *NP* particles, $\zeta = -35.3 \text{ mV}$ (as mentioned in Introduction). One may infer that the electrostatic attraction forces between *NP* particles and polycation samples are the prevailing ones in the separation process. The differences that could be observed in their removal effectiveness may be due to their different chemical structure which results from the polyfunctional amines used in their synthesis, DMAPA for PCA_{20} and TETA for PCT_{20} . Thus, the higher functionality of TETA (10) than that of DMDAP (4) leads to a higher branching degree of PCT_{20} than that of PCA_{20} . This is revealed by the viscometric behavior of both polymers in water (Figure 5).

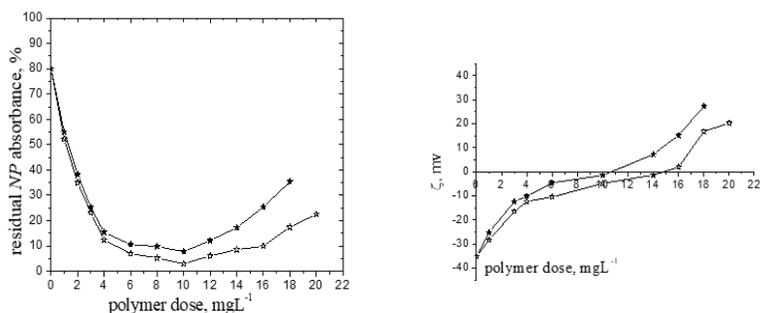


Figure 4: The residual NP absorbance (%) (a) and zeta potential (ζ) (b) dependence on the polymer dose for PCA_{20} (solid star) and PCT_{20} (empty star); settling time 120 min.

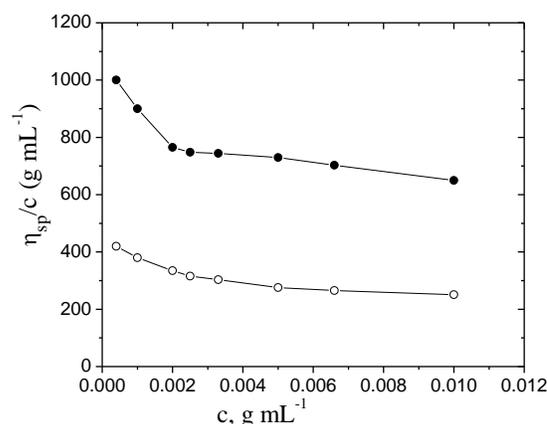


Figure 5: Reduced viscosity, η_{sp}/c , dependence on the polymer concentration, c : PCA_{20} (solid circle) and PCT_{20} (empty circle).

The smaller increase of the reduced viscosity values at high dilution for PCT_{20} than for PCA_{20} indicates a lower chain expansion of the former polymer than that of the latter one. Based on this finding one would have expected that PCA_{20} to be a more efficient flocculant than PCT_{20} ; the greater chain expansion, the greater is the probability of interaction with pesticide particles. On the contrary, one observes that the *NP* removal efficiency is higher in the presence of PCT_{20} than in the presence of PCA_{20} , over the entire poly-

mer dose interval investigated. The maximum *NP* removal degree was noticed at the same polymer dose ($\text{dose}_{\text{op}} = 10 \text{ mg L}^{-1}$) for both polyelectrolytes, but it was higher for PCT_{20} (97%) than for PCA_{20} (92%). This result can be attributed to: 1. the branched structure of PCT_{20} ; the branches extend into the solution, increasing the possibility of interaction between polymer segments and pesticide particles. The branching reactions take place at the secondary amine groups and lead, mainly, to formation of the tertiary amine groups [24]; 2. the high solubility of Dimethoate in water, 39.8 g L^{-1} [25], and hence to the important contribution of hydrogen bonding established between the amide units of Dimethoate and some secondary and/or tertiary amine groups of PCT_{20} to the pesticide removal. This assumption is sustained by zeta potential measurements (Figure 4b). Thus, over the *FW*, ζ gets values between -10.5 mV and 2 mV. It is well recognized that in case of the simple charge neutralization flocculation mechanism, the optimum dose corresponds to zeta potential close to zero Kleimann et al. (2005) [26]. This is the case of PCA_{20} where over *FW*, ζ values between -4.6 and -1.5 mV have been recorded.

In closing this discussion we would like to stress that both synthetic polyelectrolytes have slightly better removal efficiency for *NP* particles (between 92% and 97%) than the pullulan derivatives and CS (removal efficiency between 90%-92%) [17,18].

5.1.2 Removal of *Dc* Pesticide Formulation: The flocculation performance of PCA_{20} and PCT_{20} was also tested on the removal of *Dc* from synthetic emulsion; this pesticide formulation contains the active ingredient Deltamethrin, which is [(S)-Cyano-(3-phenoxyphenyl)-methyl] (1R,3R)-3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropane-1-carboxylate. The results are presented in Figure 6a. Both polyelectrolytes exhibit close values of the removal efficiency over the dosage range investigated. The minimum residual *Dc* absorbance, below 10%, has been noticed in the polycation dose interval between 1.4 mg L^{-1} and 1.8 mg L^{-1} for PCA_{20} and between 1.4 mg L^{-1} and 2 mg L^{-1} for PCT_{20} . The zeta potential measurement performed on initial *Dc* emulsion gave a negative value, $\zeta = -28.2 \text{ mV}$. Based on this result, one surmises that the *Dc* particles are attracted by the cationic sites of the ionic polymers investigated by means of the electrostatic forces, and hence their separation from the model emulsions. This assumption is sustained by the curves in Figure 6b which presents the zeta potential evolution as a function of polycation dose.

Irrespective of the polyelectrolyte, ζ values have risen over the entire domain of polycation doses investigated, from the initial emulsion negative value (see above) to positive ones, namely 25 mV (PCA_{20}) and 20 mV (PCT_{20}). ζ reached values close to zero (between -4.0 mV and 0.2 mV) for PCA_{20} and (between -4.8 mV and 0.5 mV) for PCT_{20} in the optimum polycation dose interval, that indicates the charge neutralization mechanism for *Dc* particles removal by these polyelectrolytes.

One has also to emphasize that for the *Dc* particles dispersed in water, the synthetic polyelectrolytes proved to be better flocculants than the cationic polysaccharide with 1-(2-hydroxypropyl)-3-methyl imidazolium chloride groups attached to dextran (D40-MeIm36) [27]; *FW* is located between 1.4 mg L^{-1} - 2 mg L^{-1} in case of the former group of polycations and between 2.5 mg L^{-1} - 3.5 mg L^{-1} in case of the latter one. One reason for the difference between the performances of these polyelectrolytes is the lower content of cationic groups of the dextran derivative (36%) against the synthetic polyelectrolytes (80%). The great impact of the charge content on the *Dc* removal is enforced by the similar efficacy in removal of *Dc* (more than 90% in *FW*: between 1.3 mg L^{-1} - 2 mg L^{-1}) observed in case of the polyelectrolytes with almost the same content of cationic groups, CS (85%) [16], PCA_{20} and PCT_{20} (80%).

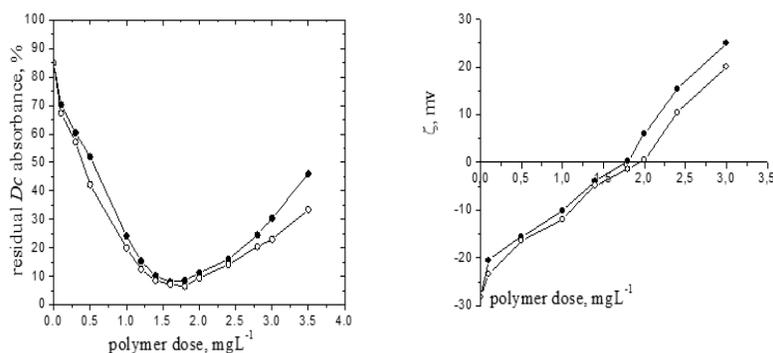


Figure 6: The residual *Dc* absorbance (%) (a) and zeta potential (ζ) (b) dependence on the polymer dose for PCA_{20} (solid circle) and PCT_{20} (empty circle); settling time 1200 min.

5.2. Chitosan (CS): Influence of Molecular Mass (*M*)

In systems where the bridging mechanism prevails, the increase in *M*, enhances the flocculation efficiency, irrespective of the ionic groups content [28], while in systems where the separation takes place by means of the patch or neutralization mechanisms, the effect of this parameter is unclear. So far, there is no report regarding the influence of *M* on the reduction of any type of pesticide content. Therefore, in order to study the effect of this parameter on the *NP* and *Dc* particle separation efficiency, three CS samples with M_v of 189, 347, 600 kg mol^{-1} have been tested. The results are presented in (Figure 7).

CS with M_v 189 kg mol^{-1} has already been demonstrated to be an efficacy flocculant for both *NP* [18] and *Dc* [16] pesticides; both electrostatic interactions and hydrogen bondings contributed to the pesticide particles separation. The data mentioned above have been introduced in Figure 7 to make it easier for the reader to track the impact of *M* on the reduction of pesticides particles content from emulsions. The three chitosan samples had a similar effect on the *NP* (Figure 7a) and *Dc* (Figure 7b) particles removal, namely the residual pesticides absorbance (%) declined with increasing CS dose, the maximum removal efficiency been recorded at the next doses: *FW* (mg L^{-1}) between 4-6 for CS189 and for CS341 and between 4-7 for CS608 in case of *NP* and between 1.3-1.6 for all the

chitosan samples in case of *Dc*. The chitosan sample with higher M_v separated *NP* particles in a larger *FW* than the samples with lower M_v , but no significantly decrease of the residual content (%) of both pesticides particles (between 90-92 for *NP* and around 90 for *Dc*) was noticed in the range of molar mass investigated; this means that the charge neutralization mechanism dominates the separation process.

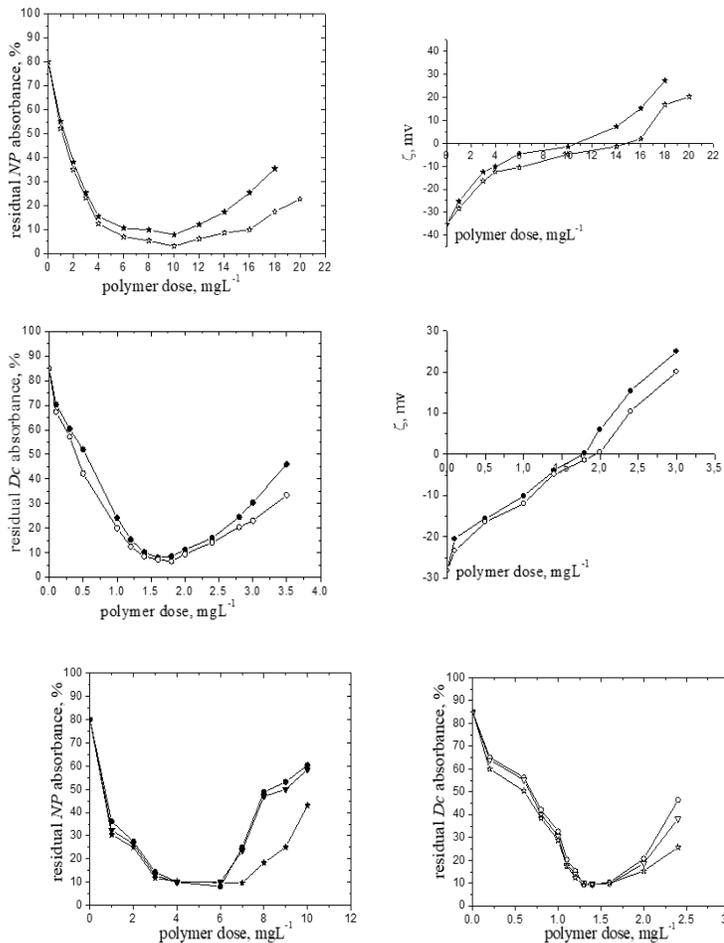


Figure 7: The residual *NP* (a) and *Dc* (b) absorbance (%) dependence on the polymer dose for CS with different M_v (kg mol^{-1}): CS189 (circle); CS347 (inverted triangle); CS 600 (star); (solid symbol (*NP*); empty symbols (*Dc*)); settling time 120 min (*NP*) and 1200 min (*Dc*).

6. Conclusion

The commercial pesticide formulations Novadim Progress (*NP*) and Decis (*Dc*) have been separated from the synthetic emulsions by aqueous solutions of some synthetic cationic polyelectrolytes and chitosan of different molecular masses and the results can be outlined as follows:

(i) Both synthetic cationic polyelectrolytes exhibited high flocculation efficiency (more than 90% pesticide removal) at low *FW*, irrespective of the nature of pesticide

(ii) For both pesticides, larger *FW* were noticed for PCT_{20} than PCA_{20} : (6 mg L^{-1} - 16 mg L^{-1}) against (6 mg L^{-1} - 10 mg L^{-1}) in the case of *NP* and (1.4 mg L^{-1} - 2 mg L^{-1}) against (1.4 mg L^{-1} - 1.8 mg L^{-1}) for *Dc*

(iii) Zeta potential measurements point out the charge neutralization as the main mechanism contributing to the separation of *NP* and *Dc* particles. Nevertheless, the hydrogen bonding's has to be taken under consideration in separation of *NP* particles by PCT

(iv) No important effect of M_v on the removal efficacy of pesticides was observed in the range of molecular masses investigated, meaning that the "charge neutralization" dominates the pesticide particles separation process.

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