

Use of dispersed and beads chitosan in liquid effluents treatment

Dihia Aili ^a, Ibrahim Feraoun ^a, Lydia Adour ^{a,b}, Hakim Lounici ^{b,c *}

^a Département de Chimie, Faculté des Sciences, Université Mouloud Mammeri, 15000 Tizi-Ouzou, Algeria

^b Unité de Recherche en Ingénierie & Environnement (URIE), Ecole Nationale Polytechnique, 10 Avenue Hassen Badi, El-Harrach, BP 182, 16200 Alger, Algeria

^c Université de Bouira, MDD, Campus Pole Technologique, 10000 Bouira, Algeria

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ABSTRACT

Chitosan, an amino-biopolymer, has received a great deal of attention in the last decades in the treatment of various suspensions and solutions for the removal of particulate and dissolved contaminants. The advantage of chitosan over other polysaccharides is that its polymeric structure allows specific modifications without too many difficulties. It is commonly prepared by deacetylating chitin in alkali solution. Contrarily to bibliography, two low temperatures (25 ± 2 and 30 ± 2 °C) and several days (10-15) have been chosen for deacetylation of purified chitins (chemical and biological). The aim was to produce soluble chitosan in diluted acetic acid solution (1%) and applying the chitosan in dispersed and gel beads forms for liquid effluents treatment as adsorbent for the removal of dye (Direct blue 71) from synthetic effluent (first application) and as biofloculant for the capture of particulate suspension from drinking water plant effluent (second application) and for the improved settling of biological colloids such as bacteria from activated sludge after biological treatment of wastewaters (third application). This study demonstrated that chitosan prepared in soft deacetylation condition has conserved its high affinity for many classes of contaminants such as humic substances, inorganic matters, suspended solids, dye molecules and bacterial suspensions. Good results were obtained for the maximal reduction of turbidity and suspension matter at very lower concentration of dispersed biopolymer (1 mg/L and 1.5 mg/L in two effluents, respectively) and for the total removal of color in natural medium pH by adsorption at a ratio: 1g of beads/50ml of dye solution. Chitosans prepared in this study are all efficient if used dispersed and gels.

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1. Introduction

Water pollution results from all human activities: domestic, industrial and agricultural, but it is also due to synthetic substances produced by chemistry [1]. When water is polluted, decontamination becomes necessary. The best purification approach is sought to reach the decontamination objectives required by law. The literature reports a multitude of processes for the treatment of contaminated water and wastewater [2-7]. However, many of the available processes proposed cannot be used at an industrial scale for technological and especially economic reasons.

Inorganic and organic wastes produced by human activities (domestic, industrial and agricultural) as well as the excessive use of synthetic substances produced by chemistry [1] have resulted in high volumes of contaminated water which threatens human health and other living organisms [8].

Discharge of colored substances into water bodies can, not only aesthetically cause issues, but also harmful to biological organisms and ecology [9]. Textile industries and other dyeing industries such as paper, printing, leather, food and plastic are major industrial wastewater sources. Generally, the volume of discharged wastewater from each step of a textile operation is approximately at a high rate of between 40 and 65 L/kg of the product [10]. The presence of dyes in textile wastewater is an environmental problem

* Corresponding author. E-mail address: hakim_lounici@yahoo.ca

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due to their high visibility, resistance and toxic impact [11]. Even low concentration of dye in water is easily visible and can reduce photosynthetic activities in aquatic environments by preventing the penetration of light and oxygen [12]. Given their synthetic origin and complex aromatic structures, dyes are non-biodegradable substances that remain stable under different conditions [13]. In this case, common methods for removing dyes are either economically unfavorable and/or technically complicated.

It is now recognized that adsorption using low-cost adsorbents is an effective and economic method for water decontamination. Much attention has recently been focused on various biosorbent materials such as fungal or bacterial biomass and biopolymers that can be obtained in large quantities and that are harmless to nature. Special attention has been given to polysaccharides such as chitosan, a natural aminopolymer.

It is clear from the literature that the biosorption of dyes using chitosan is one of the more frequently reported emerging methods for the removal of this pollutant.

Guibal's group [14-21] published a series of papers on the ability of chitosan to act as an effective coagulant to treat not only particulate suspensions but also dissolved substances. In particular, they showed that color can be removed either by adsorption onto solid-state chitosan or by coagulation/flocculation using dissolved-state chitosan.

Vakili et al. [22] have concentrated on developing materials based on natural polymers such as chitosan to serve as alternative adsorbents with improved adsorption capacity and not compromising the low cost [23]. Chitosan based adsorbents have received a lot of attention for adsorption of dyes [24]. Various modifications of this polysaccharide have been investigated to improve the adsorption properties as well as mechanical and physical characteristics of chitosan.

Due to its biodegradability and no residual toxicity, its polyelectrolytic nature, its solubility in acidic solutions [25-27] and its tendency to flocculation, chitosan is also able to overcome the nuisances of traditional coagulants/flocculants. According to its excellent intrinsic characteristics such as: high cationic charge density, its outstanding chelation behavior [28-30], long polymer chains, bridging of aggregates and precipitation (in neutral or alkaline pH conditions), chitosan is very recommended in the removal of various contaminants including both particulate and dissolved substances. These properties have been exploited to the treatment of various effluents using coagulation/flocculation such as: food, seafood and fish processing wastes [31-36], wastewater from milk processing plant [37], brewery wastewater [38], surimi wash water [39], inorganic suspensions (bentonite, kaolinite) [40-42], bacterial suspensions [43-45], effluents containing humic substances [46,47], effluents containing dyes [48,49], pulp and paper mill wastewater [50,54], olive oil wastewater [55-57], oil-in-water emulsions [58], aquaculture wastewater [59], effluent containing metal ions [60-62], effluent containing phenol derivatives [63], partially purified sewage [64], raw drinking water [65], solid suspensions from various food processing wastes [66], brackish water [67], latex particles [68], microorganisms [69], and the treatment of dyes in liquid effluents [70].

Chitosan is a linear copolymer of D-glucosamine and N-acetyl-D-glucosamine produced by the deacetylation of chitin, a natural polymer of major importance [71,72]. Chitin is the second most

abundant biopolymer in the world, after cellulose. The main sources exploited are two marine crustaceans, shrimps and crabs. Chitosan has unique properties among biopolymers especially due to the presence of primary amino groups. Moreover, it is a commercially interesting compound because of its high nitrogen content in comparison to cellulose [71].

This study tests chitosan obtained by soft deacetylation condition, as bioflocculant (from dispersed chitosan), in effluent of Taksebt drinking water treatment plant, in mixed liquor of urban wastewater treatment plant and as biosorbent (from beads chitosan) in dye treatment of synthetic water.

2. Materials and methods

2.1. Materials

2.1.1. Direct blue 71

The azo dye Direct blue 71 (DB 71), molecular formula: $C_{40}H_{28}N_7NaO_{13}S_4$ (molecular weight: 1029.9 g/mol) C.I. 34140, was chosen as adsorbate. The dye was supplied by a textile industry. Fig. 1 displays the structure of this dye. A stock solution of DB 71 at 1000 mg/L was prepared, which was diluted to required different initial concentrations: 10, 50, 100, 200 and 300 mg/L. The concentration of DB 71 in textile wastewaters is 50 mg/L [73,74].

2.1.2. Commercial flocculants

Commercial chitosan, purchased from Fluka, was used in this study and noted ChitoCom. It is commonly prepared by deacetylating chitin using 40-50% aqueous alkali at 110-115 °C for a few hours [75]. It comes from a chitin shell crab and was characterized by a low molecular weight.

A synthetic anionic polymer AN 910 used by Taksebt drinking water treatment plant was employed in the present work.

2.1.3. Biological material: chitin extracted from shrimp wastes

This polysaccharide used in the experiments is coming from different purification modes: (1) commercial chitin, purchased from Fluka and noted ChitiCom; (2) chemical chitin extracted from shrimp shell by chemical treatment as described by Kadouche [76] and noted ChitiChem; (3) biological chitin extracted from shrimp shell by biological treatment as described by Arbia et al. [77] and noted ChitiBio.

2.1.4. Backwashing water of Taksebt treatment plant

Washing water collected from Taksebt drinking water treatment plant presents a turbidity situated between 300 and 400 NTU, a pH of 7-8, a conductivity of 400 μ S/cm and a UV absorbance at 254nm of 0.15. All samples were analyzed at the same day of collection.

2.1.5. Mixed liquor of wastewater treatment from Est Tizi-ouzou city plant

The samples are collected in the outlet of aeration tank. They represent the mixed liquor suspended solids (TSS) at the end of biological treatment just before the passage through the clarifier. The characteristic properties are situated between 4800 and 5500 mg/L of TSS, 7.6-8.2 of pH and 820-950 μ S/cm of conductivity.

In conventional well-settling activated sludge, the flocs often have a core structure formed by the filaments of filamentous bacteria. However, these filaments may grow to project out of the flocs. If this growth continues, they may form a bridge between adjacent flocs and prevent their independent motion. The different forms that the flocs of activated sludge can take are related to various settlement problems.

The changes in process variables, including sludge loading, nutrient concentration and oxygen concentration are responsible of various settlement problems such as deflocculation, pin-point floc, foaming and foam formation and filamentous bulking. Promotion of sludge settling may also be attempted by the addition of lime, iron salts or synthetic organic polymers.

2.2. Methods

2.2.1. Deacetylation condition of chitin

Chitosan was obtained by the deacetylation of chitin which was made by alkaline hydrolysis: an amount of chitin, as presented above, is suspended in 40% NaOH at two temperatures (25 and 30°C) during various days (Table 1). The obtained chitosan was then filtered, washed with distilled water until pH stability and oven-dried at 50 °C for 24h. The samples of chitin deacetylated are noted Chiti DA.

Table 1 - Conditions of chitin deacetylation.

Mode	T (°C)	Time (day)	Notation
Chemical	25	11	ChitiChem ^a DA 11dT25
Chemical	25	13	ChitiChem ^a DA 13dT25
Chemical	30	10	ChitiChem ^a DA 10dT30
Chemical	30	11	ChitiChem ^a DA 11dT30
Chemical	30	13	ChitiCom ^b DA 13dT30
Chemical	30	15	ChitiCom ^b DA 15dT30
Biological	25	11	ChitiBio ^c DA 11dT25
Biological	30	10	ChitiBio ^c DA 10dT30
Biological	30	13	ChitiBio ^c DA 13dT30

^a: [76]; ^b: commercial chitin (Fluka); ^c: [77]

2.2.2. Preparation of chitosan solution for coagulation-flocculation tests

100 mg of chitosan (commercial and deacetylated chitin) were dissolved in 1 mL of acetic acid (85% (w/w)) under agitation and subsequently hydrated overnight in 99 mL of demineralized water [78]. The final polymer solution was maintained at pH 4. One dose of polymer solution was tested: 1 mg of dispersed chitosan per liter of Taksebt effluent optimized in previous study (results not published) and 1.5 mg of dispersed chitosan per liter of mixed liquor optimized in our study and presented by Belksir et al. [79].

2.2.3. Preparation of chitosan beads for decolorization

The preparation of chitosan beads involves two steps: (i) chitosan dissolution and (ii) beads formation.

(i) 1.5 g of chitosan (commercial and deacetylated chitin) were dissolved in 25 mL of acetic acid solution (2N). The aqueous solution

was diluted to 100 mL by middle stirring of 3 to 4 h, and then let it stay still for 1 to 2 h.

(ii) In an ice bath, the above solution was poured into a burette equipped with a syringe 20G. 20 mL of the chitosan (commercial and deacetylated chitin) solution were dropped from the burette into a 150 mL aqueous solution of NaOH (2N). The chitosan droplets formed a bead shape in the solution. It was left in the aqueous solution for more than 24 h. The filtered chitosan beads were washed by distilled water and stored for later use. The diameter of the beads was measured with an electronic foot slides (Stainless Hardened (mm/inch)).

2.2.4. Coagulation flocculation experiments (Jar Tests)

Coagulation-flocculation experiments were carried out through a conventional Jar Test (Janke and Hunkeler) having 5 agitators and trains with variable speed. Each train is equipped with a 1 L beaker. As soon as a fixed amount of the chitosan (commercial and deacetylated chitin) solution was added to the suspension, the mixture was strongly stirred at 200 rpm during 3 min for wash waters and 250 rpm during 3 min for mixed liquor (coagulation phase). This step was followed by a slow mixing at 45 rpm during 20 min for wash waters and 50 rpm during 20 min for mixed liquor (flocculation phase) [78]. Thereafter, the solution was allowed to settle for 60 min. 25 mL of the supernatant were taken at different settling times and measured by a Hach spectrophotometer for turbidity level, TSS, pH and conductivity.

The experimental conditions should be chosen to simulate real wastewater: ambient temperature (25±2°C) and natural pH (7-8).

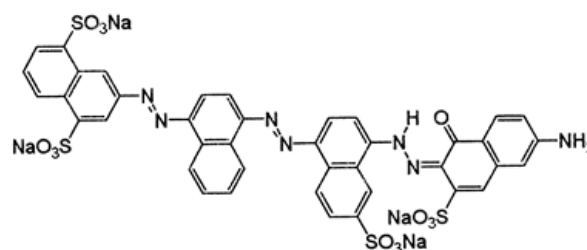


Fig. 1. Chemical structure of Direct Blue 71.

2.2.5. Batch decolorization studies

In batch adsorption kinetic experiments, 1 g of wet chitosan beads and 25 mL of dye solution were mixed in a 50 mL flask and manually stirred at ambient temperature (25±3 °C). The DB 71 dye concentration was determined at a wavelength of 587 nm by a UV-vis. spectrometer (Jasco V-530) at pH 6.5.

The experimental conditions have been conducted at ambient temperature (25±2 °C) and natural pH (6.2), in accordance with Soleymani [80].

Stirring is an important parameter in adsorption phenomena, influencing the distribution of the solute in bulk solution and the formation of the external boundary film. The Uzun's work [81] indicated that there is a small effect of shaking rate on the adsorption of two model dyes by chitosan. Wu et al. [82] also noted that agitation had little effect on adsorption. Therefore, in this study, experiments were performed without stirring.

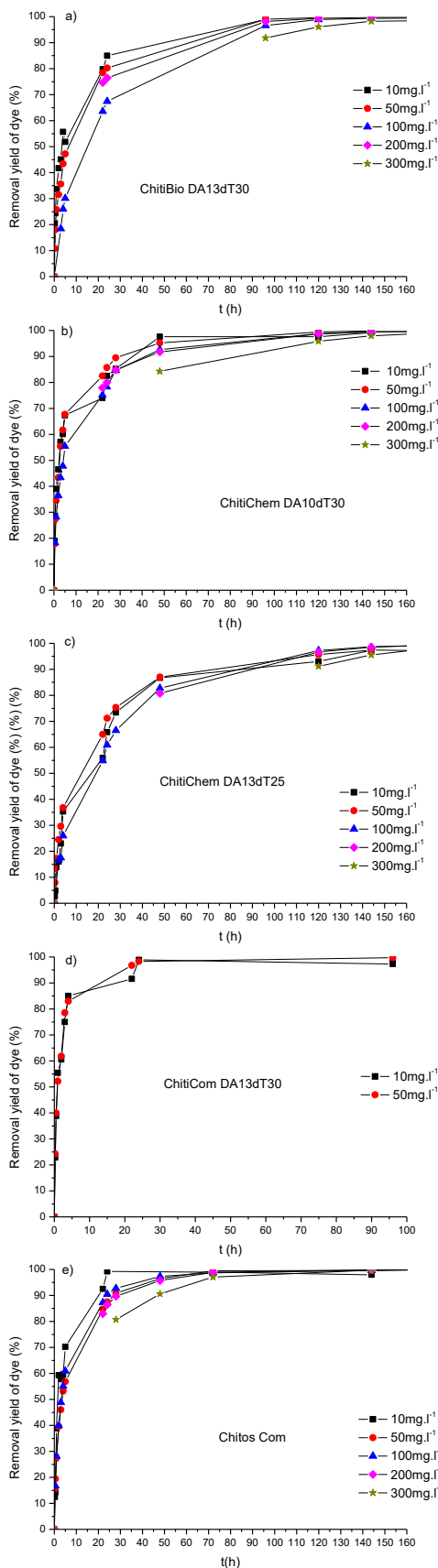


Fig. 2. Evolution of dye removal yield with contact time at different initial dye concentrations (10–300 mg/L).

Chiou and Li [83] reported that the adsorption rate on wet beads is much faster than that on dry beads and the time lag to reach similar adsorption capacity is lower because it takes time for the dry beads to swell before adsorption can take place. The same result was reported by Chang and Juang [84].

3. Results and discussion

3.1. Effect of chitosan beads on DB 71 removal

Chitosan beads are preferred since flake and powder forms of polymer are not suitable for use as adsorbents due to their low surface area and lack of porosity, as indicated by Varma et al. [85]. Chang and Juang [84] and Crini et al. [86] reported that bead-type chitosan gives a higher capacity for dye adsorption than the flake type by a factor of 2–4 depending on the source of fishery waste [82]. The authors explained this result by the fact that the beads possessed a greater surface area (i.e., more loose pore structure) than the flakes. Guibal et al. [87] indicated that it would be interesting to use chitosan gel beads instead of flakes since the production of gel beads decreases the residual crystallinity of polymer, which enhances both porosity and diffusion properties of the material, due to the expansion of the chitosan network and the increase in the specific surface area.

The chitosan beads (commercial and all deacetylated chitins prepared in this work) were spherical, except for ChitiCom DA 13dT30, rigid and presenting various diameters (Table 2).

Table 2 - Characteristics of formed beads (total weight, diameter) for commercial chitosan and different deacetylated chitins.

Chitosans	Total beads weight (g)	Average beads diameter (mm)
ChitosCom	11.64	1.76-2.29
ChitiChem DA10dT30	11.51	2.07-2.79
ChitiChem DA13dT25	11.65	1.81-2.17
ChitiBio DA13dT30	11.6	1.85-2.27
ChitiCom DA13dT30	10.15	Not spherical

Two parameters are studied: contact time and initial concentration of DB 71. Contact time is an important parameter in adsorption processes. Usually, the adsorption capacity and the removal efficiency of dyes by chitosan become higher when prolonging the contact time. However, in practice, it is necessary to optimize the contact time, considering the efficiency of desorption and regeneration of the adsorbent.

The effect of contact time upon DB 71 removal by deacetylated chitin (ChitiChim DA 10dT30, ChitiChim DA 13dT25, ChitiBio DA 13dT30 and ChitiCom DA 13dT30) and by commercial chitosan (ChitosCom) is presented in Fig. 2. The removal rate increased with the increase of time with all deacetylated chitins as well as with ChitosCom. It reaches a maximum recovery above 98% within 150 h (Fig. 2) with all initial dye concentrations varying from 10 to 300 mg/L. Thus, in these conditions, the contact time and adsorption rate are not dependent on the initial DB 71 concentration. These results contradict those of some researchers. Gibbs et al. [88] observed that increasing the initial dye concentration increased the

time required for complete recovery of the dye. This indicates that a large interval of initial dye concentration plays an important role in the removal efficiency of DB 71 on the chitosan beads.

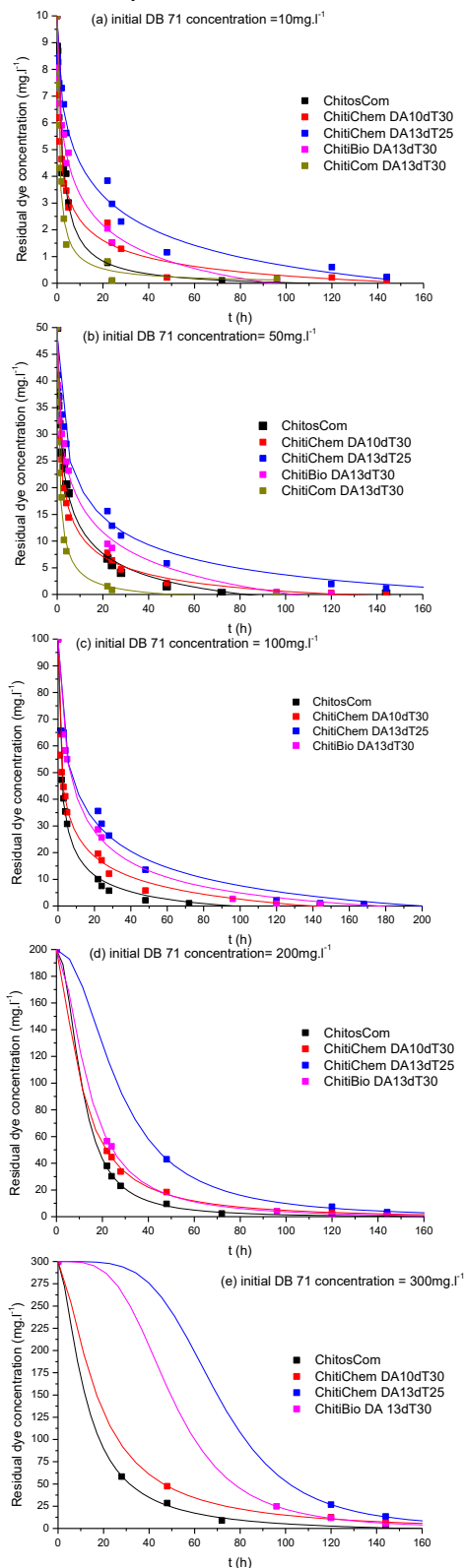


Fig. 3. Evolution of residual dye concentration with contact time at different deacetylated chitins and commercial chitosan with all initials concentrations.

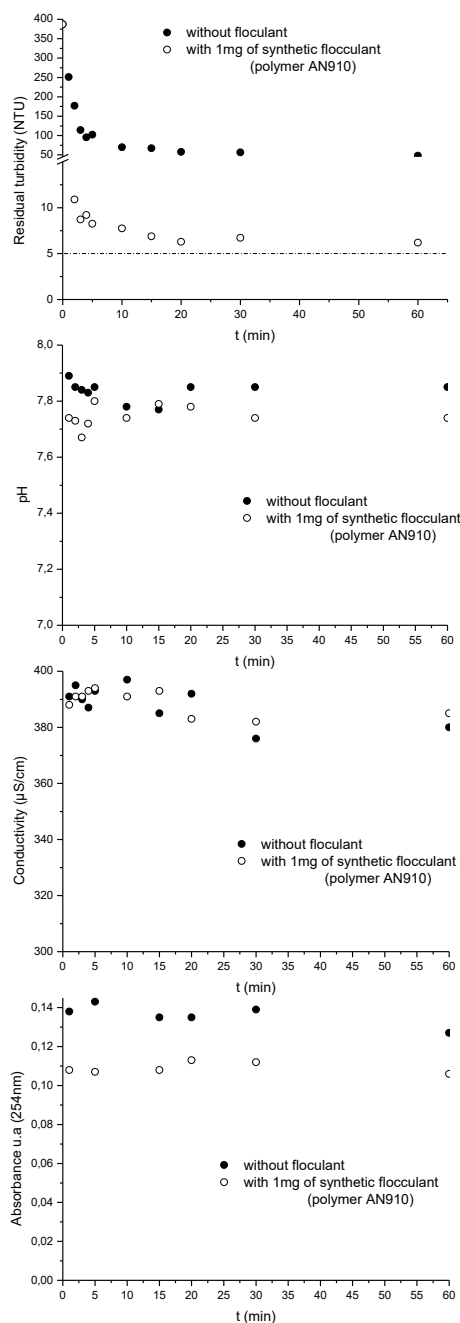


Fig. 4. Evolution kinetics of turbidity, pH, conductivity and absorbance at 254 nm without and with flocculant and anionic polymer.

The kinetic curves show two phases: at the beginning, the dye ions were adsorbed by the exterior surface of chitosan beads, and the adsorption rate was fast (almost 5 h). When the adsorption on the exterior surface reached saturation, the DB 71 dye ions entered into the pores of the beads and are adsorbed onto the interior surface of the adsorbent. This phenomenon takes relatively long contact time (almost few days). The time profile of dye uptake is single, smooth and continuous, but not leading to saturation. The equilibrium was not attained under these operating conditions.

Thus, it is necessary to increase the DB 71 initial concentration or to decrease the amount of chitosan wet beads in solution.

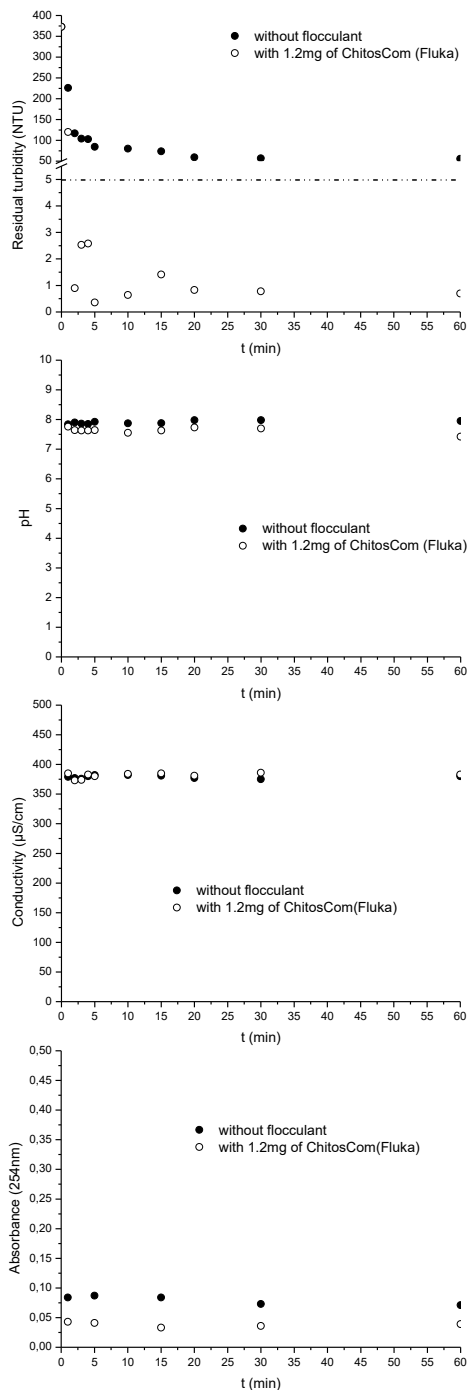


Fig. 5. Evolution kinetics of turbidity, pH, conductivity and absorbance at 254nm without and with commercial chitosan.

The presence of even small amounts of dyes (below 1 mg/L) is clearly visible and influences considerably the water quality [89,90]. After 150 h of contact time, residual concentration of DB71 (Fig. 3) depends on initial dye concentration (C_0): below 1 mg/L for $C_0 = 10$

mg/L, below 5 mg/L for $C_0 = 50$ mg/L, below 10 mg/L for $C_0 = 100$ and 200 mg/L and below 20 mg/L for $C_0 = 300$ mg/L.

At pH 6.2, the amine groups of chitosan molecules are protonated to form $-NH_3^+$ [91], thereby increasing electrostatic attractions between dye molecules and adsorption sites and causing the observed removal of the dye.

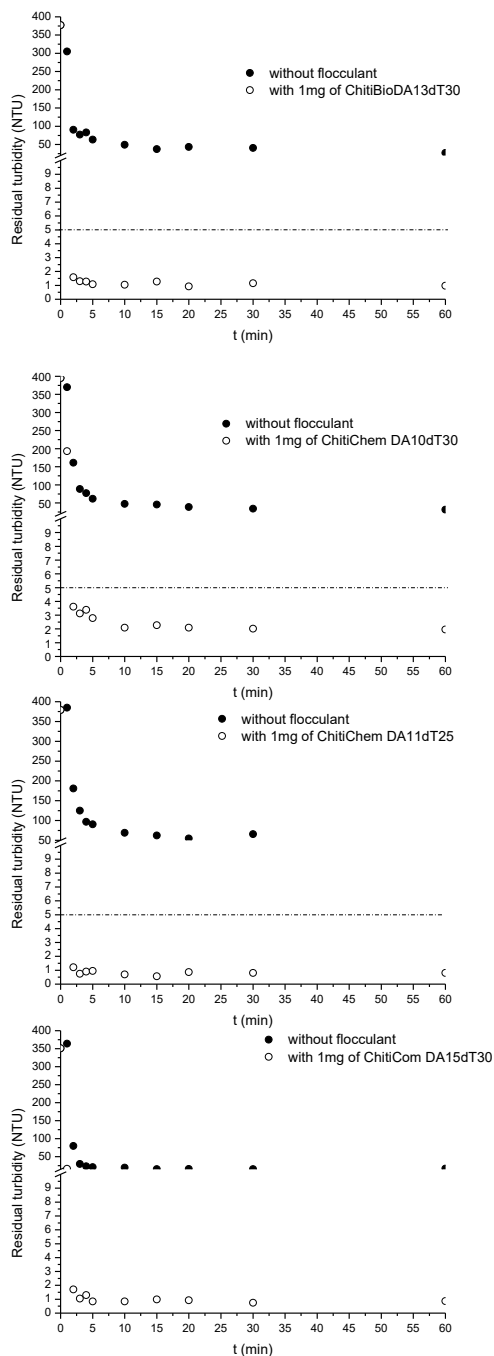


Fig. 6. Evolution kinetics of turbidity with deacetylated chitins.

The above result is in agreement with the literature: at neutral pH, about 50% of total amine groups remain protonated and theoretically available for the adsorption of dyes. The existence of free amine groups may cause direct complexation of dyes co-

existing with anionic species, depending on the charge of the dye. Guibal et al. [92] showed that not all the amino groups are really available or at least accessible. The weakly porous structure of the polymer and its residual crystallinity are critical parameters for the hydration and the accessibility to adsorption sites.

Additionally, it was important to note that no variation of pH solution was observed during adsorption process.

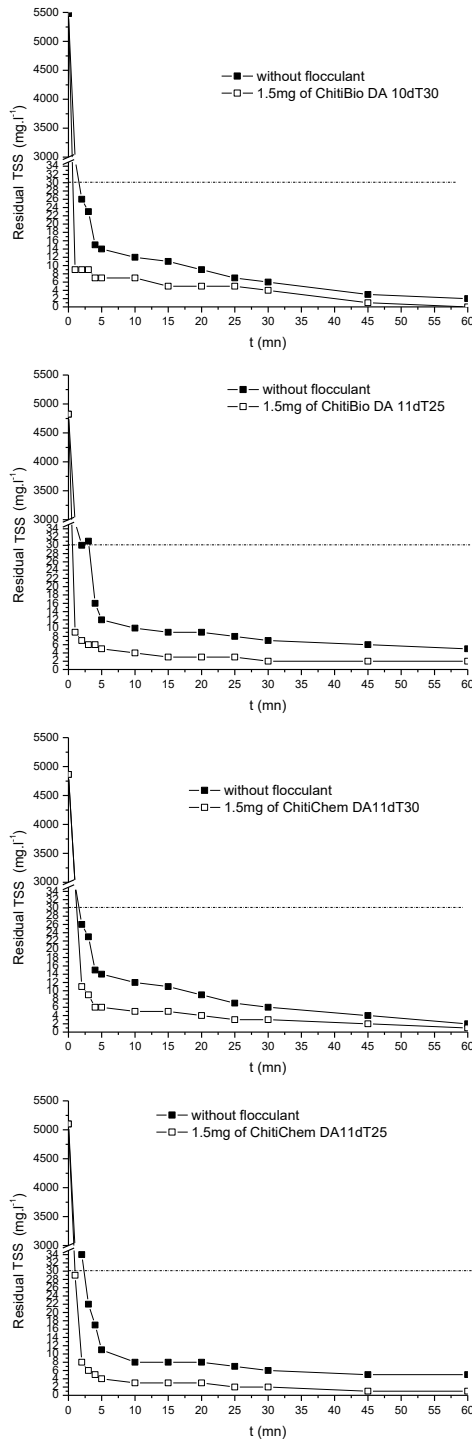


Fig. 7. Evolution kinetics of TSS with deacetylated chitins.

3.2. Effect of dispersed chitosan on washing water treatment of Taksebt plant

Without flocculant, turbidity decreases rapidly from 376 to 102 NTU within 5 min and then, slowly decreases to reach 60 NTU at the end of treatment (1 h) (Fig. 4). The wash water contained settling matters such as silica. Natural settling is not efficient because residual turbidity is higher than the norm (5 NTU for treated water).

When 1 mg of anionic polymer (AN 910) is added in 1 L of effluent, turbidity rapidly decreases from 376 to 8 NTU within 5 min and then, slowly decreases to reach 6 NTU at the end of treatment (1 h) (Fig. 4). After 24 h, no return to stabilization was observed. Residual turbidity is near the norm (5 NTU) using the synthetic polymer AN 910.

In the presence of anionic polymer, pH and conductivity (Fig. 4) values do not change over time. They are situated in the same interval obtained without flocculant: 7.5-8 and 375-400 $\mu\text{S}/\text{cm}$, respectively. The UV absorbance value at 254 nm do not vary with time (0.11 with flocculant and 0.14 without flocculant). Polymer reduces humic substances from water.

With 1 mg of commercial chitosan (Fluka) added to 1 L of effluent, turbidity decreases rapidly from 376 to 1 NTU within 5 min and then, decreases very slowly for reaching 0.98 NTU at the end of treatment (1 h) (Fig. 5). After 24 h, return to stabilization was not observed. Residual turbidity (0.98 NTU) obtained with ChitosCom is below the norm (5 NTU) contrarily to plant polymer (6 NTU) and to natural settling (60 NTU). The amino polysaccharide is very efficient if compared to synthetic polymer in treatment of filters washing waters. The pH is situated at lower values (7-7.5) than its value for anionic polymer and without flocculant (7.5-8). For conductivity and UV absorbance at 254 nm (Fig. 5), the values are the same as with synthetic polymer. These parameters remain constant with time.

Coagulation-flocculation of washing water with addition of 1 mg of deacetylated chitin (ChitiBio DA13dT30, ChitiChem DA10dT30, ChitiChem DA11dT25 and ChitiCom DA15dT30) in 1 L of effluent produced a very low residual turbidity (1 NTU) within 5 min, this value remains constant until the end of treatment (1 h) (Fig. 6) and also during 24 h. In our experiments, all chitosans cited previously and ChitosCom (Fluka) conducted in 5 min to a similar yield removal of turbidity (up to 99.7%). Consequently, deacetylation conditions (temperature and duration) have no effect on flocculant properties. The results of pH, conductivity and absorbance at 254 nm with all chitosans are identical to commercial chitosan (data not presented).

It was important to notice that 1 mg of dispersed chitosan added to 1 L of liquid effluent (in acidic condition) does not modify the pH and does not increase the organic matters concentration.

3.3. Effect of dispersed chitosan on mixed liquor of wastewater treatment from Est Tizi-ouzou city plant

Without flocculant addition, settling test was established for each coagulation-flocculation experiment. The average residual TSS demonstrated a rapidly decrease in the first minutes: 67 mg/L after 1 min, 29 mg/L after 2 min, 25 mg/L after 3 min, 16 mg/L after 4 min and 13 mg/L after 5 min (Fig. 7). After this time, a slowly

decrease was obtained reaching 9 mg/L after 20 min and 5 mg/L after 60 min.

The addition of 1.5 mg of all deacetylated chitins (ChitiBio DA10dT30, ChitiBio DA11dT25, ChitiChem DA11dT30 and ChitiChem DA11dT25) in 1 L decreases rapidly the residual TSS concentration, below 9 mg/L, only after the beginning of settling (1 min) (Fig.7). After 1 min, it decreases slowly and stabilizes to a value lower than 1 mg/L after 1 h. Thus, deacetylated chitin in our conditions can highly reduce the time and the final TSS concentration.

In natural settling, treated water approaches the norm of TSS (30 mg/L) within few minutes. However, in coagulation-flocculation with amino polysaccharide, the residual TSS was lower and obtained instantaneously.

Strand et al. [93], applying chitosan to flocculate bacterial suspensions, pointed out the predominant role of bridging in the flocculation mechanism.

3.4. Efficiency of deacetylated chitins obtained in soft conditions

The products of deacetylation have an extremely high affinity for many classes of contaminants, in accordance with several authors that demonstrated outstanding removal properties for natural organic matter [94], humic substances [95-99], inorganic suspensions [14,100,101], dye molecules [92], metal cations [61,82], proteins [38], phenolic and aromatic derivatives [88], oil and grease [55-58], bacteria [93,97], algal suspensions [98] and pathogens [59].

Chitosan becomes a soluble cationic polymer with high charge density [72,102]. Thus, treatment of chitosan with acetic acid produces a high number of protonated amine groups along the chain and this facilitates electrostatic interactions between polymer chains and the negatively charged contaminants in the treated effluents (dyes, organic compounds, etc.). It is the consequence of a low residual turbidity in the treated effluent.

In the coagulation/flocculation process, the settling rate of the formed flocs is also important since it influences the overall cost and efficiency [102]. It is known that the addition of flocculant has a significant effect on the settling time. With chitosan, the increase of floc size favors the floc settling rate and reduces consequently the settling time.

4. Conclusion

This work has demonstrated that the similar chitosans in their both states: dissolved or solid (beads form) can be a potential substitute for metallic salts and synthetic polyelectrolytes in the treatment of various wastewater for the removal of both particulate and dissolved substances (suspended solids, Direct blue 71 dye and bacterial suspension).

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