

## Valorization of marine waste in sludge treatment from tizi-ouzou wastewater treatment plant

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### ABSTRACT/RESUME

**Abstract:** This study involves on valorization of Algerian marine waste, shrimp shells, in treatment of urban sludge (organic) by coagulation-flocculation / filtration. So, transformation of chitin into chitosan has been realized in laboratory in order to make a bioflocculant. Therefore, chitosan prepared had been tested for conditioning of urban sludge from Tizi-Ouzou wastewater treatment plant. The results indicate that chitosan shows a biocoagulation-bioflocculation behavior which is similar to standard chitosan.

### I. Introduction

The increase of shellfish production in world led to increase of volume in co-products. The disposal of such waste has always been expensive and had often a harmful environmental impact. Indeed, for a long time, shellfish canneries produced large volumes of wastes that were not recycled and were simply thrown in the nature creating major problems of pollution near to production sites. However, to technical progress and to markets' development, it has become possible now to transform wastes into useful and marketable products. Their main way for recycling is production of chitin, one of the major compounds of crustacean cuticles [1]. In its native form, chitin has no use. Nevertheless, after processing, it finds an interesting use in various fields. By chitin deacetylation, its obtain chitosan that is a polycationic biopolymer formed of D-glucosamine units and N-acetyl-D-glucosamine, non-toxic, biodegradable and biocompatible; soluble on diluted organic acids [2, 3].

The industrial production of chitosan is described in Figure 1 and it essentially includes 04 successive steps (demineralization, deproteinization, bleaching and deacetylation) [4]. Therefore, the cost of bioflocculant is expensive. Reducing these steps into one (just deacetylation) or two steps

(demineralization followed by deacetylation) has been considered in this work in order to minimize chitosan manufacturing cost. From shell of shrimps *Parapenaeus longirostris*, 02 Chitosans were prepared and applied in biological conditioning of urban thick sludge collected from Tizi-Ouzou wastewater treatment plan.

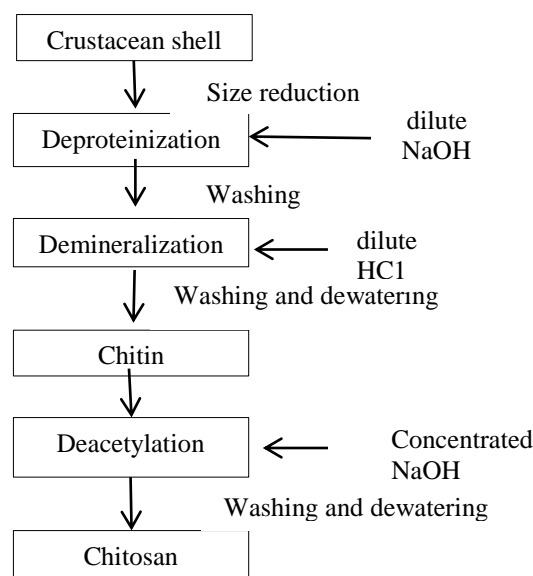


Figure 1. Conventional diagram of chitin and chitosan processing [4].

## II. Materials and methods

### II.1. Materials

- Acetic acid 99-100 % purity,  $d = 1.5$  (analar NORMAPUR).
- Sodium hydroxide (BIOCHEM Chemopharma).
- Standard Chitosan (Fluka). It is symbolized by ChitosCom.
- Shell shrimp *Parapenaeus longirostris* collected from Azzefoun region in Algerian.
- Sludge samples collected, in May 2014, at exit from thickener of Tizi-Ouzou wastewater treatment plant (Algeria).

### II.2. Methods

#### II.2.1. Preparation of raw shell

Before use, the flesh, antennas and legs were removed from the shrimp shells. They were, then, boiled in water for 1 hour to remove the maximum amount of flesh. Thereafter, they were dried at  $163^{\circ}\text{C}$  for 1h in a drying oven. After cooling, the shells were subjected to a thermal shock and facilitate crushing. The Raw Shell is symbolized by RS.

#### II.2.2. Preparation of chitosans and solubility test

Two bioflocculants were prepared in laboratory. The first one is obtained by deacetylation of RS in 40% NaOH for 7 days at temperature  $30^{\circ}\text{C}$ , so it is symbolized by RSDA7dT30. The second one is obtained by demineralization of RS in HCl 1.5N for 1 hour at ambient temperature ( $20^{\circ}\text{C}$ ) (conditions optimized in Kadouche work's [5]), followed by deacetylation in NaOH 40% for 7 days at temperature  $30^{\circ}\text{C}$ , so it is symbolized by RSDMDA7dT30.

In order to test solubility, 50mg of each product (RSDA7dT30 and RSDMDA7dT30) were dissolved in 50ml of acetic acid at 1% (v/v) [6].

#### II.2.3. Conditioning of urban sludge by chitosans

In order to identify the nature of urban sludge taken from Tizi-Ouzou wastewater treatment plant, various parameters were evaluated as Dry Matter (DM), Volatile Dry Matter (VDM), dryness of sludge and pH. [7]

Sludge conditioning was carried out by flocculation using motor mechanical agitation (MR3001 K). 300ml of sludge in 600 ml of beaker mixed with each bioflocculant at different dose from 0.5 to 2mg of dispersed product per grams of DM. The mixture was agitated at 250 rpm for 20 seconds (coagulation phase). The agitation rate is subsequently reduced to 50 rpm for 2 minutes (flocculation phase) [8]. The sludge dehydration step was carried out by filtration under vacuum until obtaining of sludge characterized by dryness.

## III. Results and discussion

### III.1. Solubility test of products

This test demonstrated that deacetylation (during 7days at  $30^{\circ}\text{C}$ ) of RS with and without demineralization conducted to products soluble in diluted acetic acid. This property is very important for using as coagulant-flocculant.

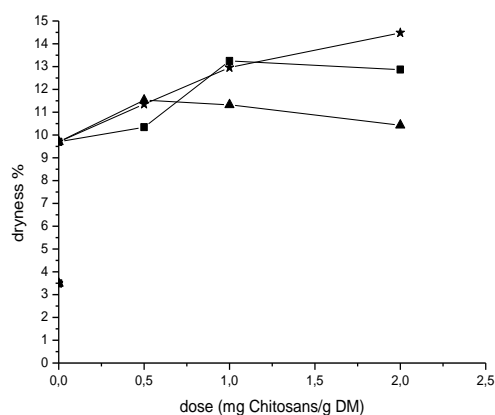
### III.2. Physico-chemical sludge characterization

The characteristics of sludge are measured at  $22^{\circ}\text{C}$ . The sludge has a pH of 7.2; a dryness of 3.5% corresponding to 96.5% of humidity and a dry matter concentration of 34.6 g/l. The ratio VDM/DM is about 40% so the urban sludge nature is organic. A cationic polyelectrolytic is recommended for sludge treatment.

### III.3. Conditioning of urban sludge

#### III.3.1. Influence of chitosan dose on cake dryness

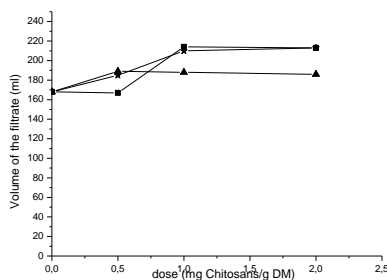
Figure 2 shows the evolution of cake dryness in relation with dose of each flocculant. Without adding flocculant, the filtered sludge has a dryness of 9.68%. After adding flocculants, it is observed that a significant improvement in cake dryness. With RSDMDA7dT30, an increase occurs for all doses used (0.5- 2 mg / g DM) and this result is very comparable to standard chitosan. But with RSDA7dT30, an increase was occurred only for weak dose and beyond strong doses, dryness is not improved. 2mg of RSDMDA7dT30/g DM give a maximal improvement of about 50% compared to without flocculant. In contrairely, 0.5mg of RSDA7dT30/g DM and 1mg of ChitosCom/g DM are improved of 18.8% and 36.7%, respectively. According to [9], the conditioning of Baraki City urban sludge by coagulation- flocculation followed by centrifugation or filtration under pressure, leads to maximum dryness of 17.42% and 35.01 % at doses of 1.73mg and 4.8mg of ChitosCom/ g DM, respectively.



**Figure 2.** Variation of cake dryness with chitosan dose for each flocculant RSDMDA7dT30 (★), RSDA7dT30 (▲) and ChitosCom (■).

### III.3.2. Influence of chitosan dose on filtrate volume

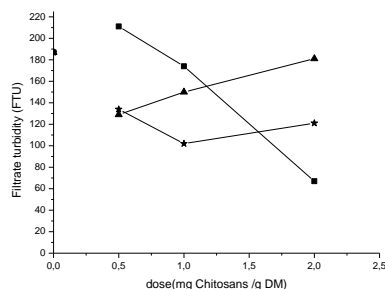
Figure 3 shows the evolution of filtrate volume depending on dose for each chitosan. In absence of a flocculant, the filtrate volume is 168ml. The addition of 1mg of ChitosCom and 2mg of RSDMDA7dT30 /g DM both increased the volume of filtrate to a maximum of 214ml. 188ml are obtained with 0.5mg of RSDA7dT30 /g DM. Beyond these doses, there is no change in filtrate volume. The product RSDMDA7dT30 presents a similar dehydration to standard chitosan. The increase on filtrate volume corresponds to an increase of dryness cake.



**Figure 3.** Variation of filtrate volume with chitosan dose for each flocculant RSDMDA7dT30 ( ★ ), RSDA7dT30 ( ▲ ) and ChitosCom ( ■ ).

### III.3.3. Influence of chitosan dose on filtrate turbidity

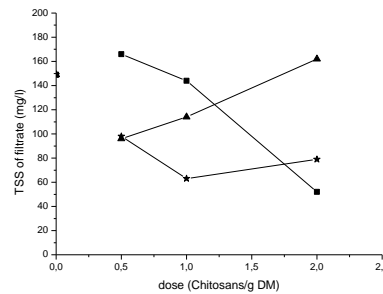
Figure 4 shows the modification of a physicochemical parameter (turbidity) of filtrate when various chitosans were added to wet sludge. The filtrate turbidity always remains under that without addition of flocculating agent. The chitosans prepared in this study are a good coagulant-flocculant.



**Figure 4.** Variation of filtrate turbidity with chitosan dose for each flocculant RSDMDA7dT30 ( ★ ), RSDA7dT30 ( ▲ ) and ChitosCom ( ■ ).

### III.3.4. Influence of chitosan dose on filtrate suspension matter

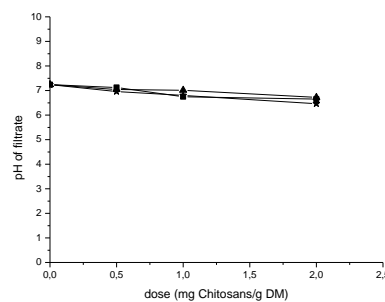
Figure 5 shows a same evolution of filtrate suspension matter (symbolized by TSS) with turbidity.



**Figure 5.** Variation of filtrate suspension matter with chitosan dose for each flocculant RSDMDA7dT30 ( ★ ), RSDA7dT30 ( ▲ ) and ChitosCom ( ■ ).

### III.3.5. Influence of chitosan dose on filtrate pH

Figure 6 shows the evolution of filtrate pH depending on dose of each chitosans (ChitosCom, RSDMDA7dT30 and RSDA7dT30). The initial pH of non-filtered sludge was 7.20. In absence of flocculant, the filtrate pH remains stable (7.24). By adding of different chitosans, the filtrate pH decreases slightly until it is set between 6.04 and 7.06, depending on dose used. This low acidification is due to acetic acid (1%) used to solubilize the chitosan.



**Figure 6.** Variation of filtrate pH with chitosan dose for each flocculant RSDMDA7dT30 ( ★ ), RSDA7dT30 ( ▲ ) and ChitosCom ( ■ ).

## IV. Conclusion

The valorization of the shrimp's exoskeletons *Parapanaeus longirostris* by producing chitosan in 01 or 02 steps is then possible. The obtained results on conditioned sludge showed that prepared chitosan and standard chitosan had enabled to improve sludge dryness (11.5% with 0.5mg of RSDA7dT30/g of DM, 14.48% with 2mg of

RSDMDA7dT30/g of DM and 13.23% with 1mg of chitoscom /g DM). It is 9.68% without flocculant. This result is followed by a reduction in turbidity and suspension matter of filtrate while pH remains nearly invariable. The use of chitosan as bioflocculant agent is recommended in conditioning- filtration of organic urban sludge. This study demonstrates the feasibility in the use of partially pure chitosan in the conditioning of sewage sludge. In the future, an optimization of the coagulation-flocculation parameters is necessary.

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## VI. Abbreviations

**Chitoscom:** Standard Chitosan (Fluka)

**DA:** Deacetylation

**DM:** dry matter

**pH:** potential of hydrogen

**rpm:** revolutions per minute

**RS:** raw shell

**RSDA7dT30:** deacetylation of raw shell for 7 days at temperature 30°C

**RSDMDA7dT30:** demineralization of raw shell followed by deacetylation for 7 days at temperature 30°C

**T:** temperature

**TSS:** total suspended solids

**VDM:** volatile dry matter

■ : ChitosCom

★ : RSDMDA7dT30

▲ : RSDA7dT30

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