Chitosan use in chemical conditioning for dewatering municipal-activated sludge
H. Zemmouri, N. Mameri and H. Lounici

ABSTRACT
This work aims to evaluate the potential use of chitosan as an eco-friendly flocculant in chemical conditioning of municipal-activated sludge. Chitosan effectiveness was compared with synthetic cationic polyelectrolyte Sedipur CF802 (Sed CF802) and ferric chloride (FeCl₃). In this context, raw sludge samples from Beni-Messous wastewater treatment plant (WWTP) were tested. The classic jar test method was used to condition sludge samples. Capillary suction time (CST), specific resistance to filtration (SRF), cakes dry solid content and filtrate turbidity were analyzed to determine filterability, dewatering capacity of conditioned sludge and the optimum dose of each conditioner. Data exhibit that chitosan, FeCl₃ and Sed CF802 improve sludge dewatering. Optimum dosages of chitosan, Sed CF802 and FeCl₃ allowing CST values of 6, 5 and 9 s, were found, respectively, between 2–3, 1.5–3 and 6 kg/t ds. Both polymers have shown faster water removal with more permeable sludge. SRF values were 0.634 × 10¹², 0.932 × 10¹² and 2 × 10¹² m/kg for Sed CF802, chitosan and FeCl₃ respectively. A reduction of 94.68 and 87.85% of the filtrate turbidity was obtained with optimal dosage of chitosan and Sed CF802, respectively. In contrast, 54.18% of turbidity abatement has been obtained using optimal dosage of FeCl₃.

Key words | chemical conditioning, chitosan, FeCl₃, Sed CF802, sludge dewatering

INTRODUCTION
Sludge, derived from municipal wastewater treatment plants (WWTPs), is a heterogeneous mixture of 50–80% of pollution which contains a high-organic load, colloids, pathogenic germs, mineral particles, cations and heavy metals (Li & Ganczarczyk 1990). These characteristics impact negatively on sludge dewatering. Also, they can pose a serious environmental risk if sludge disposal is inadequately managed. Hence, the main target of sludge treatment is to produce clean bio-solids that could be used beneficially later. The moisture content of final sludge has to be limited for lower costs, and to decrease environmentally harmful impacts caused by pathogenic organisms (Appels et al. 2008; Tuan et al. 2012). On the other hand, sludge is also a valuable source for the reuse of inorganic material and energy production.

To improve sludge dewatering characteristics and promote the separation of flocs from the liquid phase to achieve a high dry solid content, sludge requires an efficient conditioning which can be a biological, chemical or physical treatment. Chemical conditioning consists of adding chemical reagents to the sludge in order to assemble the dispersed colloidal particles in larger flocs which further facilitate the solid-liquid separation (Qi et al. 2011). Depending on the nature of the solids to be treated, chemical conditioning can reduce, through coagulation flocculation process, 90–99% incoming moisture content to 65–85% (Lee & Liu 2000). Flocculation is one of the most widely used cost-effective techniques for sludge conditioning (Harif et al. 2012).

Vast categories of materials used as conditioner agents can be classified broadly into two categories: inorganic and organic. The inorganic chemicals (commonly used are ferric and aluminum salts) effectively flocculate sludge leading to very hard dewaterable and compressible slurry (Qi et al. 2011). The organic materials are further classified into natural and synthetic. The synthetic ones may be cationic, anionic or non-ionic. In most cases, they are derived from oil-based and non-renewable raw materials (Suopajärvi et al. 2015). A new class of polymeric flocculants, i.e., the graft copolymers (synthesized from natural and synthetic
polymers) has been developed (Lee et al. 2014). These materials have gained a great popularity as sludge conditioners thanks to their ease in handling, lower mass content, small storage space requirements and their ability to increase sludge/liquid separation (Lee et al. 2014). However, some of these products often lead to secondary pollution and new environmental problems (Renault et al. 2011). The sludge formed has a limited potential for recycling due to its non-biodegradability (Zahrim et al. 2011). Its toxicity is a real problem. It is due to unreacted monomers such as acrylamide and reaction by-products of the polymers in water (Renault et al. 2011).

If they are locally available, natural polymers or biopolymers can reduce such environmental problems, reuse sludge as fertilizer with respect for the environment and encourage proper handling and disposal of sludge. So these eco-friendly flocculants can be suggested as an interesting alternative for chemical conditioning (Bolto & Gregory 2007). Indeed, compared with the traditional inorganic and synthetic organic flocculants, natural polymers are generally non-toxic and biodegradable, which is considered essential from a sustainability point of view (Wang et al. 2013).

Recently, an increasing interest has been shown in developing biomaterials. Latterly these include modified starches, celluloses, chitosan, and microbial materials produced by micro-organisms as well as bacteria, fungi and yeast (Bolto & Gregory 2007). Technically, these bio-products are easy to use, do not endanger the handler and they have a wider effective dosage range for flocculation of colloidal suspensions (Renault et al. 2011). Moreover, sludge treated with bio-flocculants can be reused on agricultural land (Seki et al. 2010).

Chitosan could be highlighted as one of the most natural promising cationic biopolymers for intense applications, especially solutions in sludge conditioning. Chitosan is a β-(1 → 4) linked polysaccharide made up of d-glucosamine residue [poly-β-(1→4)-D-glucosamine]. It is partially an N-deacetylated derivative by the alkaline deacetylation of chitin (Renault et al. 2011). This latter is the second most abundant natural biopolymer next to cellulose. Chitin is the main component of crustacean shells and marine arthropods (Nomanbhay & Palanisamy 2005). It is a linear hydrophilic amino-polysaccharide with a rigid structure containing both glucosamine and acetyl-glucosamine units. Chitosan differs from chitin by the amine groups (-NH2). Chitosan is insoluble in water but soluble in dilute organic acids such as acetic acid and formic acid and inorganic acids (exceptionally sulfuric acid) where the free amino groups are protonated and the biopolymer becomes fully soluble. These groups give to chitosan an interesting cationic character in acidic medium (Chen et al. 2005). With long polymer chains and high molecular weight, chitosan behaves as an effective coagulant and/or flocculant for the removal of contaminants from water and wastewater.

Owing to its non-toxicity, biocompatibility, and biodegradability and multi-functional properties (e.g., polyelectrolytic nature, ability to form intermolecular hydrogen bonds, efficient against bacteria, viruses, fungi and tendency to flocculation) (Renault et al. 2011), chitosan has gained a large application in versatile area of water and wastewater treatment, namely colloidal particles (Huang et al. 2000), organic matter (Cheng et al. 2005), micro-organisms (Strand et al. 2005), treatment of dyes in effluents (Guibal & Roussy 2007), organic matter in pulp and paper mill wastewater (Rodrigues et al. 2008), textile wastewater (Szygula et al. 2009), heavy metals and phenolic compounds in cardboardmill wastewater (Renault et al. 2009), surface water treatment (Zemmouri et al. 2011) and inorganic suspensions in kaolinite suspension (Li et al. 2015). However, chitosan use in water treatment may be a crucial issue since its cost is higher than the use of synthetic flocculants; that is why the optimization method of De Fao et al. (2008) based on cost seems inapplicable. In fact, chitosan is expensive due to its high extraction cost (Naznin et al. 2005; Arbia et al. 2015). This is one reason (among others) which may explain the difficulty to transfer such technologies from the laboratory to industry.

Very modest information is currently available on the application of chitosan as an environmentally friendly compound in sludge conditioning from wastewater treatment. For these reasons, current research aims to examine the potential application and operating characteristics of chitosan as biopolymer in conditioning of municipal sludge. Chitosan efficiency is compared to synthetic cationic polymer, i.e., Sediipur CF802 (Sed CF802) and ferric chloride. For this purpose, raw sludge samples from Beni-Messous WWTP were conditioned with chitosan, Sed CF802 and ferric chloride. For this purpose, raw sludge samples from Beni-Messous WWTP were conditioned with chitosan, Sed CF802 and ferric chloride (FeCl3) using the classic jar test method. To determine filterability, dewatering capacity of conditioned sludge and the optimum dose of each conditioner, capillary suction time (CST), specific resistance to filtration (SRF), cakes dry solid content and filtrate turbidity were examined.

**MATERIALS AND METHODS**

**Sludge provenance**

Sludge samples were collected in triplicate (to improve the representativeness) from the stabilization tank of a...
Beni-Messous municipal WWTP located 15 km west of Algiers, Algeria. The treatment process at this station is carried out by activated sludge of medium loads, with a capacity of 50,400 m³/d. The process of sludge dewatering consists of pressure filtration using filter strips. After sampling, sludge was passed through a 4.25 mm sieve to remove any gross-sized particles. It was stored at 4 °C for maximum 3 days of sampling to prevent the aging process and for reducing the effect of biochemical composition change. Before testing, a 500 mL sludge sample was acclimatized for 30 min at room temperature in the laboratory. The characteristic values of the raw sludge are summarized in Table 1.

**Conditioners**

Cationic polyelectrolyte Sed CF802, FeCl₃ and chitosan were used for sludge conditioning trials. Chitosan was supplied by SIGMA-ALDRICH: C3646-256. It came from crab shell chitin and was characterized by a viscosity of 100 Pa·s and a degree of deacetylation greater than 75%. It is solid in beige color. Chitosan was dissolved in acetic acid with stirring at room temperature. The proportions adopted are as follows: 100 mg of chitosan/1 mL acetic acid 80% w/w completed to 100 mL with demineralized water. The final polymer solution was maintained at pH 4 (Zemmouri et al. 2014).

Sed CF802 properties are summarized in Table 2. Laboratory analytical grade FeCl₃ was prepared in 5% solution. All solutions of conditioning agents were freshly prepared during each experiment.

**Chemical conditioning method**

Sludge conditioning was carried out by flocculation using a Stuart Scientific Jar Test device (flocculator) with six ramps. Sludge samples of 100 mL in a 500 mL beaker were mixed with solutions containing different amounts of conditioners calculated on the basis of chemical mass per unit mass of dry solids contents of the sludge. It was expressed in kilogram per ton of dry solids (kg/t ds). The jar test was operated at 140 rpm for 20 seconds for intense mixing of the polyelectrolyte into the sludge, and then stirring speed was reduced to 28 rpm for 2 minutes to promote floc growth. Floc structures of settled sludges were observed for each trial.

**Sludge dewatering**

Pressure filtration seeks to generate flocs with good ability to dewater with the lowest specific resistance possible, high dryness sludge, clear filtrate and cake which easily detaches from the filter funnel. As a laboratory-scale mechanical dewatering device, a filter press was adopted for expressing water from conditioned sludge samples. Pressure filtration trials were carried out using a cell pressure filtration standard (APHA, AWWA & WEF 1995), specially conceived in the laboratory for this experiment. After flocculation, conditioned sludge is immediately transferred into the filtration cell. An appropriate pressure (10 kg/cm²) was applied. During the introduction of the piston, a certain amount of filtrate can flow under the effect of gravity without pressing. The filtration time was set to 1 hour.

**Analyses**

Collected filtrates were measured as function of time. Dry solids content (ds, %) of the recuperated cake and filtrate turbidity were determined according to procedures given in Standard Methods (APHA, AWWA & WEF 1995). Sludge dewaterability was evaluated using the SRF. The values of this parameter were calculated via the principle proposed by Christensen & Dick (1985). Indeed, SRF was determined from the plot of filtration time/filtrate volume (t/V) versus filtrate volume (V). Using the slope of the line of the previous characteristic, SRF was calculated from Equation (1).

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**Table 1** | Properties of raw sludge in this study before conditioning

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>8.3</td>
</tr>
<tr>
<td>Total suspended solids (TSS)</td>
<td>g/l</td>
<td>3.5</td>
</tr>
<tr>
<td>Volatile suspended solids (VSS)</td>
<td>g/l</td>
<td>17</td>
</tr>
<tr>
<td>Dry solid content</td>
<td>%</td>
<td>3.22</td>
</tr>
<tr>
<td>CST</td>
<td>s</td>
<td>48</td>
</tr>
<tr>
<td>SRF</td>
<td>10¹² m/kg</td>
<td>6.78</td>
</tr>
<tr>
<td>T</td>
<td>°C</td>
<td>25</td>
</tr>
</tbody>
</table>

**Table 2** | Characteristics of flocculants

<table>
<thead>
<tr>
<th>Flocculant</th>
<th>Sedipur CF802</th>
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</thead>
<tbody>
<tr>
<td>Abbreviation</td>
<td>Sed CF802</td>
</tr>
<tr>
<td>Ionic character</td>
<td>Cationic</td>
</tr>
<tr>
<td>Molecular weight (dalton)</td>
<td>High (250,000 million)</td>
</tr>
</tbody>
</table>
known as the Ruth’s equation describing the filtration sub-process.

\[ t = \left( \frac{\mu r w}{2 A^2 P} \right) V + \frac{\mu R f}{AP} \]  

(1)

where \( r \) is the SRF (m/kg); \( P \) is the vacuum pressure of filtration (N/m\(^2\)); \( \mu \) is the viscosity of filtrate (normally taken as that of water at filtrate temperature) (Ns/m\(^2\)); \( V \) is the volume of filtrate (m\(^3\)); \( t \) is the filtration time (s); \( w \) is the weight of dry solids per volume of filtrate (kg/m\(^3\)); \( A \) is the area of the filter paper (m\(^2\)); \( R_f \) is the resistance of filter medium (1/m).

Equation (1) supposes laminar flow, uniform solids deposition during filtration and constant increase in filtrate flow resistance as the cake increases in thickness. For compressible sludge, \( R_f \) is negligible compared to the resistance of the sludge cake. In these conditions, Equation (1) becomes

\[ t = \left( \frac{\mu r w}{2 A^2 P} \right) V = bV \]  

(2)

where \( b \) is the line slope of the characteristic \( t/V(V) \).

Finally, \( r \) can be calculated from the following formula:

\[ r = \left( \frac{2 A^2 P}{\mu w} \right) b \]  

(3)

To optimize the operation of chemical sludge conditioning, CST parameter has been evaluated according to the Standard Method 2710G (APHA, AWWA & WEF 1995) with a portable apparatus (Triton 304B; chromatography paper Whatman no. 17).

RESULTS AND DISCUSSION

CST

CST is among the most commonly used indices for filtering techniques. It is an empirical measure of the resistance offered by the sludge to the withdrawal of water. That is why CST is usually employed to characterize sludge dewaterability (the lower the CST the higher the dewatering rate).

Results of CST tests are shown in Figure 1. The CST value has been reduced from 48 s obtained in the raw sludge case, to 5 and 6 s with optimal dosage, in the range of 2–3 and 1.5–3 kg/t ds of Sed CF802 and chitosan, respectively. Beyond the optimal dosage, the CST value increases again. Otherwise, with sludge conditioned with 6 kg/t ds as optimal dose of FeCl\(_3\), CST value was around 9 s. Indeed, both cationic polyelectrolytes showed a good dewaterability.

The low CST obtained using cationic polyelectrolytes is due to smaller flocs and sludges containing less bound water. These sludges are therefore dewatered faster than those obtained with FeCl\(_3\). However, further increase in polyelectrolyte concentration increased CST. This is associated with the overdosing phenomena caused by excess polyelectrolyte remaining in the liquid phase leading to the viscosity increase and then deteriorating the sludge dewaterability (Christensen et al. 1995).

On the other hand, saturation of the colloidal surface with polymer is usually accompanied by a reversal of the surface charge. The optimal polymer dosage is commonly associated with partial coverage of the colloidal surface, accompanied by a minimum surface charge (Lee & Liu 2000).

SRF

To determine optimum dose range of cationic polyelectrolytes (chitosan and Sed CF802) and FeCl\(_3\), Figure 2 depicts the evolution of SRF data as a function of dosage of each flocculant. Initially, SRF value of unconditioned sludge was \( 6.78 \times 10^{12} \) m/kg. SRF is decreased when both cationic polyelectrolytes and FeCl\(_3\) were added. The optimum doses for Sed CF802 and chitosan were about 1.5–2 kg/t ds for both polyelectrolytes. Beyond the optimum value, the SRF increases again. SRF values of sludge conditioned with Sed CF802 and chitosan at the respective optimum doses were \( 0.634 \times 10^{12} \) m/kg and \( 0.932 \times 10^{12} \) m/kg, respectively. On the other hand, 4.5 kg/t ds of FeCl\(_3\) has reduced SRF to \( 2 \times 10^{12} \) m/kg. Through these results, the objective of this study is accomplished; adding flocculating agents improves the dewaterability of sludge, i.e., reduces the SRF.

Indeed, dewatering of unconditioned sludge containing colloidal solids (e.g., sewage sludge) is very difficult to
achieve, or even impossible. Qi et al. (2011) have reported that blinding of filter or cake support is caused by the migration of sludge fine particles into the cake pores which in turn decreases the cake porosity and increases the cake specific resistance. For this reason, a portion of the free water can never be extracted. Otherwise, an increase in pressure may drive the fine particles into the pores which have previously served for the passage of the filtrate, leading to its blocking, resulting consequently in a very low dewatering performance. So, adding chemical conditioners (organic or inorganic) like chitosan, Sed CF802 and FeCl3, in our case, have helped through coagulation flocculation process, to increase the sludge particle size by agglomerating the small fines of the sludge colloids (causing blinding), to form large flocs (which are easily separated from the water). This floc agglomeration is translated by the SRF decrease and consequently the filterability improvement.

Cake dry solid contents

Figure 3 shows the evolution of the cake dryness according to the dose of each flocculant. From the data depicted in this figure, it can be discerned that a significant increase in dryness to 17.31% with 3 kg/t ds of chitosan has been recorded and 2 kg/t ds of Sed CF802 increases cake dryness to 18.65%. The cakes formed with application of both polyelectrolytes are uniform, with thicknesses of 0.5 cm. These results led to the conclusion that the performance of these two polymers is substantially similar, with a slight difference. Otherwise, 15.78% of cake dryness was obtained using 4 kg/t ds of FeCl3.

Obtaining large flocs after flocculation is conducive to good settleability and filterability. However, the filterability does not depend on the size of the flocs. It essentially depends on floc cohesion or their mechanical and bond strengths unifying the elementary particles that make up the formed cluster (Lee & Wang 2000). The weakness of these links may result in a change in the structure of the filter cake which becomes less porous, and consequently a decrease in the rate of filtration.

Filtrate residual turbidity

In order to examine the cleaning of the filtrate and the influence of flocculants on the filtrate turbidity, filtration tests were carried out. For this purpose, the turbidity of filtrate was measured after the filtration test. The experimental results are represented in Figure 4. This shows that a maximum filtrate cleaning (minimum nephelometric turbidity unit, NTU, values) is achieved with both chitosan and Sed CF802 with 94.68% and 87.85%, respectively. In contrast, 54.18% of turbidity abatement has been obtained using FeCl3.

A better capture efficiency of some fine dispersed particles in the aqueous phase translates the lower residual turbidity of filtrate when both cationic polyelectrolytes were used. These fine, dispersed particles of sludge were flocculated to form primary flocs due to electrostatic attraction. Lee & Liu (2000) have shown that knowing that the fine

Figure 2 | SRF vs. polymers dosage.

Figure 3 | Cake dry solid content vs. polymers dosage.

Figure 4 | Turbidity removal vs. polymers dosage.
particles should cause a decrease in cake porosity, flocculation of sludge particles by the cationic polyelectrolyte could prevent fine particles from clogging up the filter. This also contributes to the enhanced dewaterability of sludge.

Coagulation flocculation mechanism induced by chitosan

The sludge particles are most frequently known to be positively or negatively charged. Chemical conditioners, often with opposite charges, are used to coagulate or flocculate sludge colloids by charge neutralization, leading to the establishment of interactions between charged particles. It is well known that the two main mechanisms of flocculation using organic polymers are the destabilization of the colloidal system by charge neutralization and bridging intra-particles (Lee et al. 2014). Polymer can adsorb on the surface of a colloidal particle due to a chemical strength (chemical bonding) or physical force (e.g., Van der Waals forces), or both. Some parts of the polymer chains can then be determined by bare paths on another particle and therefore closest to form bridges. So, destabilization of sludge is interpreted as a neutralization charge and/or particles bridging during the application of polyelectrolytes. The combined action of the mass and charge of the polymer helps to implement both phenomena bridging and charge neutralization (Gregory & Barany 2011).

The bridge allows the polymer to set a large number of particles and to include them in large flocks. Since chitosan is a cationic polyelectrolyte, we can say that the clotting mechanism is essentially borne by a double effect: charge neutralization and bridging flocs. Chitosan is adsorbed on the surface of the colloidal particles by hydrogen bonds between the negative charges of the surface of the colloidal particles and the free amine groups of the chitosan (Renault et al. 2011). The attractive electrostatic interactions between the positively charged chitosan segments and the negatively charged sites of particles promote adsorption (Gregory & Barany 2011), then the adsorbed amount of chitosan increases with the increase of the dose of added chitosan.

According to results related to the effect of the chitosan dose, the general trend shows that each increase of chitosan above its optimum concentration, increases SRF and decreases cake dry solid contents. One hypothesis for this phenomenon would be the reversal of load and re-stabilization of colloidal particles which have been coagulated. This re-stabilization of loads depends on the zeta potential of the solution (Gregory & Barany 2011). In fact, chitosan, by its constitution, has a surplus of electrical charges and was solvated by water trapping colloidal particles causing turbidity. Indeed, Gregory & Barany (2011) have reported that the excessive addition of polymer creates hyper-conductive water where collisions between particles due to electric forces are so intense, they disrupt completely the balance of the solution.

CONCLUSION

The aim of this work was to study the feasibility of chitosan application in the chemical conditioning of sewage sludge from Beni-Messous municipal WWTP. The performance of this biopolymer as a conditioner was compared with synthetic polymer (Sed CF802) and FeCl3. It is worth noting that according to physicochemical characterization, the considered sludge is highly organic in nature.

The results of this study showed that the addition of chitosan, Sed CF802 and FeCl3, with optimal dosages between 2–3, 1.5–3 and 6 kg/t ds, respectively, allowed CST values of 6, 5 and 9 s consecutively to be obtained. Beyond the optimum doses, CST increases again. Both cationic polyelectrolytes have shown faster water removal, with a permeable filter cake and hence more permeable sludge. SRF values of conditioned sludge by optimal dosages of both chitosan and Sed CF802 in the range of 1.5–2 kg/t ds and 4.5 kg/t ds of FeCl3 were, respectively, $0.952 \times 10^{12}$, $0.634 \times 10^{12}$ and $2 \times 10^{12}$ m/kg. A reduction of 94.68 and 87.85% of the filtrate turbidity was obtained with chitosan and Sed CF802 optimal dosages, respectively. In contrast, 54.18% of filtrate turbidity abatement has been obtained when applying optimal dose of FeCl3.

According to the obtained results, we can conclude that chitosan has shown the same efficiency in terms of sludge conditioning as well as synthetic polymer (Sed CF802). Compared to synthetic polymeric flocculants having the main problems of non-biodegradability and being unfriendly to the environment, chitosan as a natural organic flocculant, being environmentally friendly, safe, biodegradable and available from seafood industry waste, may be a promising substitute for conventional flocculants used so far in the field of sludge conditioning. The sole inconvenience of chitosan is its high cost, which could be minimized by future technological developments.

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