Influence of anaerobic digestion on particle surface charge and optimal polymer dosage

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Abstract Anaerobic digestion leads to significant changes of the sludge structural matrix, affecting particle size distribution and dewaterability. The surface charge, determined by means of streaming current, can be effectively used to monitor the complex phenomena of floc disruption, colloid formation and chemical conditioning. To study the relation between surface charge and optimal dosage, two different cationic polyelectrolytes were used: Praestol 644, polymer with high molecular weight and low charge density, and Poly Dadmac, with relatively low molecular weight but high charge density. The optimal Poly Dadmac dosage strictly met the value required to neutralise particle charge whereas the optimal dosage of Praestol 644 indicated that the relevant charge was considerably lower than the one required for charge neutralisation. Mechanisms of action are therefore clearly different. Another objective was to investigate the changes of dewatering characteristics of secondary sludge during anaerobic digestion tests at different inoculum content by determining charge density, and optimal polymer dosage. The optimal polyelectrolyte dosage remains almost constant during digestion at high inoculum, but a significant increase in the first period is observed at low inoculum, thus suggesting that the release of colloidal and supracolloidal material from sludge affects dewaterability, especially in the first days of digestion.
Keywords Activated sludge; anaerobic digestion; dewatering; optimal dosage; surface charge

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Introduction

The anaerobic process leads to irreversible changes of the structural matrix of sludge flocs and particles, consequently affecting particle size distribution and dewaterability. The effect of the anaerobic process on sludge dewaterability is controversial, with some studies indicating that digestion generally improves sludge dewaterability (Brooks, 1970; Lawler *et al.*, 1986), whilst other authors state that the digestion process deteriorates the dewatering capabilities of sludge (Houghton and Stephenson, 2002; Guan *et al.*, 2003; Novak *et al.*, 2003; Jin *et al.*, 2004). The sludge properties that have been shown to affect dewatering include size distribution (Karr and Keinath, 1978; Novak *et al.*, 1988), extra-cellular polymeric substances (Jin *et al.*, 2003), presence of inorganic cations such as Ca^{2+}, Mg^{2+} (Higgins and Novak, 1997) and the presence of filaments. The dewatering characteristics of the sludge can also be described by the surface charge, directly affecting the coagulation/flocculation of colloid. Flocs in activated sludge usually carry negative charge at neutral pH. It has been found that the extracellular polymeric substances (EPS), complex mixture of polymers excreted by the micororganisms, contribute to the negative surface charge of the sludge flocs (Jia *et al.*, 1996; Liao *et al.*, 2001) and thus the flocculation properties. Conditioning is therefore required to neutralise particle charge but the optimal dosage rarely coincides with that needed to keep the zeta potential at zero (Roberts and Olsson, 1975). As regards the influence of the anaerobic digestion, Jia *et al.*

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(1996) observed that during batch tests both surface charge and EPS content change significantly.

The objective of this study was to investigate the changes that occur in sludge dewaterability during batch anaerobic digestion tests. Specific attention was paid to particle charge density determined by streaming current (SC) measurements and to optimal polymer dosages. Two polyelectrolytes with different charge density and molecular weight were tested.

Materials and methods

Sample

Excess sludge was kept from the municipal Rome-North wastewater treatment plant, one of the four wastewater treatment plants of the city of Rome. The work was performed in the frame of a co-operation agreement with ACEA, the public company being in charge of the operation of the water and wastewater treatment plants of Rome municipality.

A conventional sewage-treatment process is carried out on the municipal plant based on screening, primary clarification and secondary treatment by activated sludge.

Secondary sludge was sampled before the thickener to avoid any interference of polyelectrolyte generally used in the thickener to increase its performance.

Batch digestion tests

The digestion tests were performed in reactor bottles immersed in a temperature controlled, agitated water bath at 37°C. Each bottle had a total volume of 500 mL. Sampled sludge was inoculated with digested sludge taken from the anaerobic full scale digester at two different rates: in the "low inoculum" test the inoculum percentage was 40% of total mass, in the "high inoculum" it was 75%.

The produced biogas was collected in a calibrated 1-L eudiometer tube placed on the digestion bottle via a ground-glass connection. The tube has a glass hose-coupling from which a sufficiently long hose connection leads to a levelling flask. The upper end of the eudiometer tube is fitted with a conical stopcock for adjusting the zero point. The liquid contained in the tube and in the levelling flask was NaCl at pH 3 to avoid CO_2 losses by carbonate formation (Figure 1).

To analyse the soluble phase, the particulate sludge matter was removed by centrifugation (10 min at 6,000 rpm) followed by filtration through 0.45 μm pore size membrane filters. Soluble COD (chemical oxygen demand), measured in duplicates, was determined by photometric determination of chromate consumption by the organic compounds, subsequent to digestion in concentrated sulphuric acid solution for 2 h at 148°C by means of COD Cell Test by Spectroquant Merck (EPA method 410.4). Soluble proteic COD has been calculated by means of the modified Lowry Kit for Protein Determination (Sigma-Aldrich # P 5656).

Particle charge detector

The charge density determinations were performed by a Particle Charge Detector PCD02 (Mütek GmbH, Herrsching). The PCD operates on the principle of the so-called "streaming current detector". Inside a measuring Teflon vessel, a piston moves back and forth at constant frequency in a sample. Colloids (and other adsorbable material) adhere to the piston and vessel surfaces, such that the apparent characteristics of these surfaces become those of the attached colloidal materials. Due to the oscillating piston movement, the sample liquid phase flows in the annular space between pistons and vessel wall. The resulting streaming current, referred to as SC, is detected by electrodes at opposite ends of the flow path and amplified to give a digital output. The SC is proportional to the electric

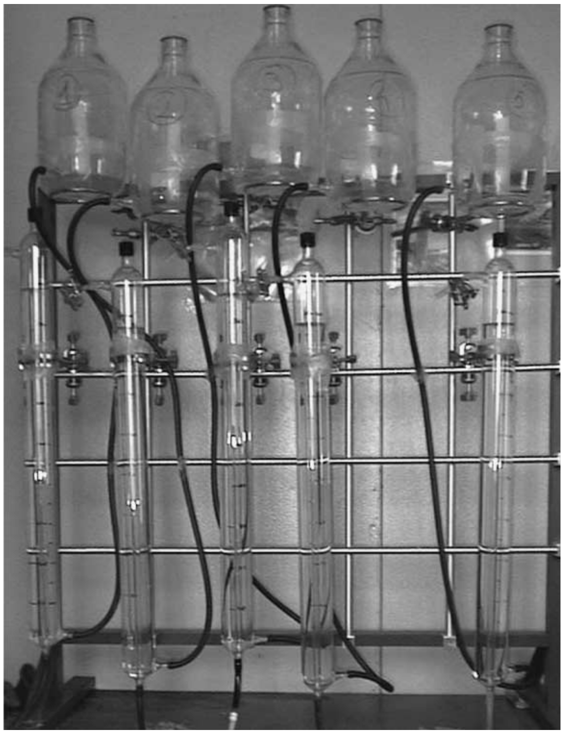

Figure 1 Experimental apparatus for biogas collection and measurement

charge of the colloids and therefore provides a measure of particle charge similarly to zeta potential (Abu-Orf and Dentel, 1997). The overall charge can be quantitatively measured by a titration using a standard polyelectrolyte solution (0.001 N polydiallyldimethylammoniumchloride solution, called Poly Dadmac). A titrant (organic polyelectrolyte) of opposite charge to the sample is added until the latter reaches the point of zero charge. The original charge amount is therefore calculated from the titrant consumption. Polymer characteristics of Poly Dadmac and of Praestol 644, commonly used for sludge conditioning, are listed in Table 1. Sludge samples were centrifuged at 5,000 rpm for 10 min and the centrate was titrated in the PCD. This procedure was used to determine the charge related to the colloidal particles. Alternatively, the charge total quantity of sludge particles was evaluated using diluted sludge samples with deionised water (1:20), thus allowing free piston movement without interference due to solid phase.

Sludge filterability and conditioning dosage

Sludge filterability was estimated using a standard capillary suction apparatus supplied by Triton Electronics Ltd., UK. Polymer conditioning tests were conducted using either of the two polymers reported in Table 1.

Table 1 Polymer characteristics

Parameter	Poly Dadmac	Praestol 644
Molecular weight (g/mol)	40,000–100,000 g/mol	$6-7\cdot10^{6}$ g/mol
Charge density (meq/g)	6.2	3.3
Charge type	Cationic	Cationic

Conditioning tests were performed in the following way: 100 mL of the sludge sample were placed into each of a series of 250 mL beakers and homogenised by mechanical stirring. Twenty millilitres of flocculant at increasing concentration were then added to sludge samples, homogenising for 30 s at 300 rpm rapid mixing and for a further 60 s at 100 rpm. CST of each conditioned sample was then determined (US EPA, 1979).

Optimal dosage was assessed as that providing the minimum in the CST-dosage curve.

Results and discussion

Dewaterability and streaming current

Dentel and Abu Orf (1993) found that the polymer (Pollu-Treat C426) optimal dosage, evaluated by CST measurements, approximately corresponded to that providing zero streaming current.

Figure 2 shows sludge conditioning tests carried out using either Praestol 644 or Poly Dadmac. Praestol provided a sharp decrease of CST and therefore its optimal dosage was considerably lower than that of Poly Dadmac. Moreover, at increasing dosages over the optimal one, a corresponding increase in CST value was observed for sludge conditioned by Praestol, but not for that conditioned by Poly Dadmac. The optimal dosages determined by CST curves were then used to calculate the superficial charge theoretically neutralised by the two polymers. The optimal Poly Dadmac dosage coincided with that required for particle charge neutralisation, as determined by titration with PCD, both for raw and digested sludge samples (values reported in Table 2 are average values of 10 replicates).

On the contrary, the optimum dosage of Praestol 644 clearly indicates that neutralised charge at the optimal dosage is considerably lower than total sludge charge. This can be explained considering that optimal dewatering might be achieved before complete surface charge neutralisation occurs, when the adsorbed polyelectrolyte extends far enough from the floc surfaces overcoming the distance over which electrostatic repulsion takes place (Csempesz *et al.*, 1998).

The flocculation dose therefore depends mainly on the nature of the polyelectrolyte and is related to the flocculation mechanism. For the low molecular weight polyelectrolyte Poly Dadmac, the optimum dose corresponds to a zero zeta potential of the flocculated sludge particles, indicating a charge neutralisation mechanism. For the ultra-high molecular weight Praestol, the optimal dose is only approximately 70% of the required Poly Dadmac dose: in this case, no complete charge neutralisation occurred, suggesting the predominance of bridging effects (Dentel, 2001).

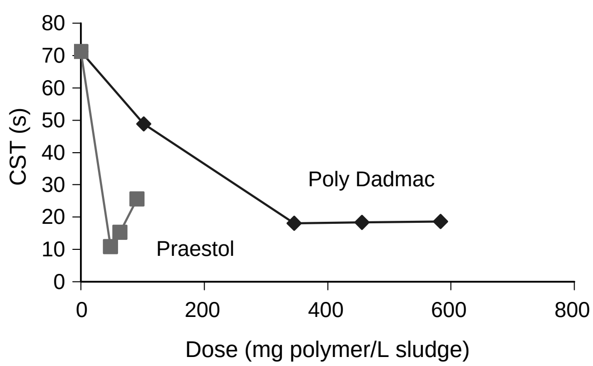

Figure 2 Conditioning tests of undigested sludge

Table 2 Comparison of particle charge (determined by PCD) and that neutralised at the optimal polymer dosage

	Particle charge determined by PCD (mC/g TS)	Particle charge neutralised at optimum Poly Dadmac dosage (mC/g TS)	Particle charge neutralised at optimum Praestol dosage (mC/g TS)
Secondary raw	4,503 ± 223	4,489 ± 302	720 ± 49
Secondary digested*	3,719 ± 191	3,717 ± 265	876 ± 71

*After 18 d of anaerobic digestion

These results indicate that polyelectrolyte molecular weight and charge density can noticeably influence dosage requirements, suggesting that the use of polymers with high molecular weight inclined to "bridging" flocculation might have economical convenience with respect to the use of polymers with low molecular weight carrying high charge.

Figure 3, showing two micrographs of sludge conditioned at the optimal dosage of Praestol and Poly Dadmac, confirms that conditioning has a great influence on sludge floc structure: while Praestol induces separation between liquid and solid phase, thus clearly distinguishing the boundary of single aggregates, the sludge structure obtained with Poly Dadmac is considerably subdivided.

Effect of digestion process on sludge dewaterability and charge density

The objective of this work was also to study the changes of dewatering characteristics of secondary sludge during a batch anaerobic digestion process at different inoculum percentages by investigating charge density, soluble proteic COD and optimal polymer dosage during the tests (Figures 4 and 5).

Sludge surface charge increases markedly during the first days at low inoculum percentage, whereas at high inoculum digestion the increase is less evident. This difference may be due to a larger floc "disintegration" and colloid release during the first digestion days at low inoculum causing an increase of specific surface and consequently of surface charge.

After the first phase, the surface charge begins to decrease, evidencing a colloidal material degradation and transformation to biogas. These findings are confirmed by the soluble protein content during the digestion. For the digestion with low inoculum, in fact, the initial significant release of proteins is followed by a degradation in the second digestion phase.

The optimal polyelectrolyte dosage determined by CST with Praestol 644 is practically constant during digestion at high inoculum (Figure 5), but significant dewatering worsening is observed in the first days at low inoculum, thus confirming that the release

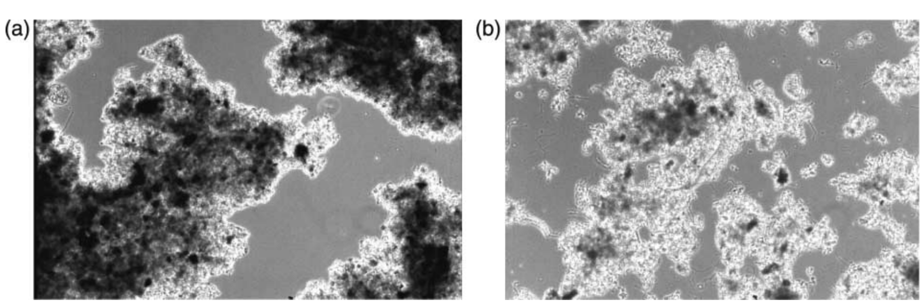

Figure 3 Sludge conditioned with optimal dosage of Praestol (a) and Poly Dadmac (b)

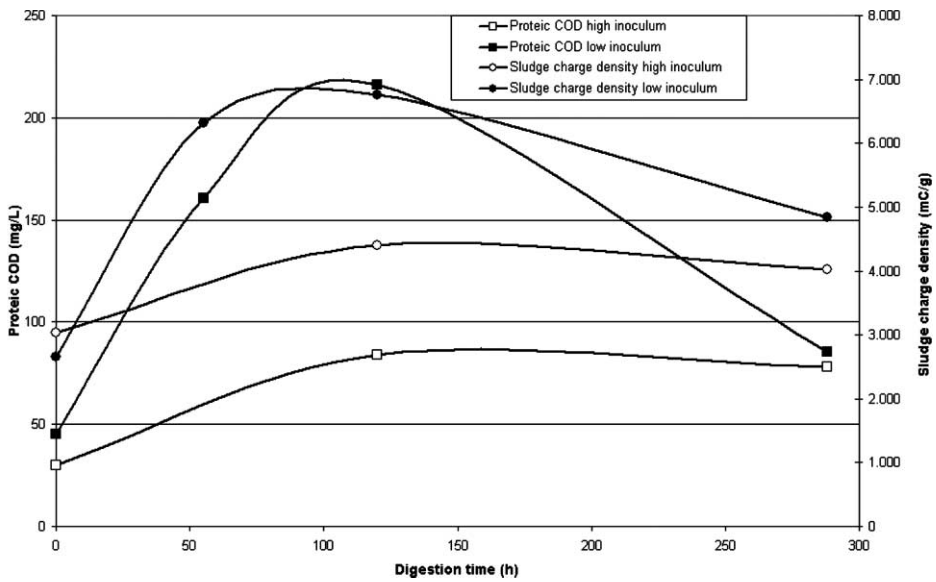

Figure 4 Proteic soluble COD and particle charge density during anaerobic digestion

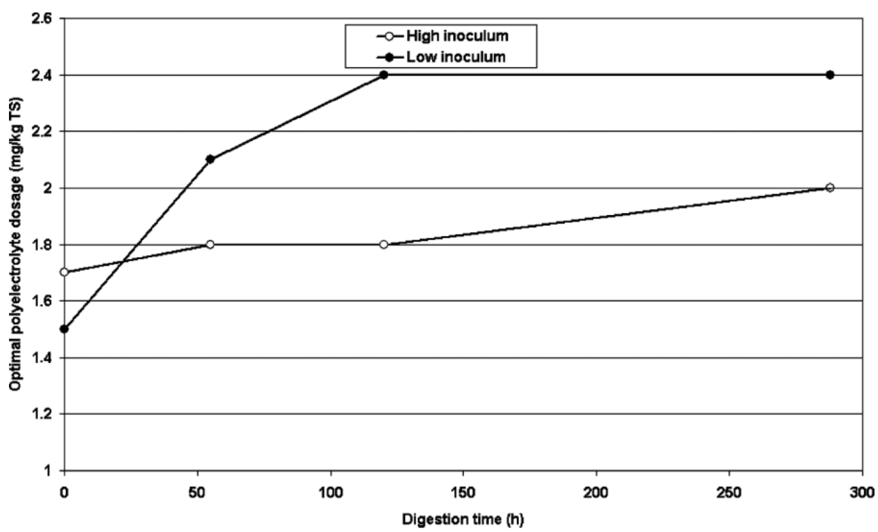

Figure 5 Optimal polymer dosage during anaerobic digestion

of colloidal and supracolloidal material affects dewaterability, especially in the first days of digestion.

The fines created by biological hydrolysis during the early stages of digestion cause deterioration of the sludge drainability In fact, fine particles blind the sludge cake and filter medium during filtration, resulting in deterioration of sludge dewaterability (Karr and Keinath, 1978).

Conclusions

The relation between sludge surface charge and optimal dosage required for sludge conditioning was investigated with two different cationic polyelectrolytes, one with high molecular weight and medium charge density (Praestol 644) and the other one with low molecular weight but high charge density. Praestol optimal dosage always resulted noticeably lower than that required with Poly Dadmac. On the basis of the polymer charge densities and their dosages, the superficial charge neutralised by sludge conditioning was calculated. The optimal Poly Dadmac dosage strictly met the value required to neutralise particle charge and, instead, the optimal dosage of Praestol 644 indicated that the relevant charge was considerably lower than the one requested for charge neutralisation. Mechanisms of action of the two polyelectrolytes are therefore clearly different: while the action of Poly Dadmac is specifically addressed to neutralise the particle charge, Praestol 644 extends far enough from the floc surfaces to overcome the distance over which electrostatic repulsion takes place. In such a way, large particles can be formed by union of elemental flocs where charges are included inside the new particle. It was therefore evident that both polyectrolyte molecular weight and charge density noticeably influence the dosage requirements in sludge flocculation.

As regards the changes of dewatering characteristics of secondary sludge during anaerobic digestion, sludge surface charge increased markedly during the first days at low inoculum percentage, whereas at high inoculum digestion the increase was less evident. This difference may be due to a larger floc "disintegration" and colloid release during the first digestion days at low inoculum causing an increase of specific surface and, consequently, of surface charge. After the first phase, the surface charge begins to decrease, evidencing a colloidal material degradation and transformation to biogas. These findings are confirmed by the soluble protein content during the digestion. For the digestion with low inoculum, in fact, the initial significant release of proteins is followed by a degradation in the second digestion phase.

The optimal polyelectrolyte dosage is almost constant during digestion at high inoculum, but a significant increase in the first period is observed at low inoculum, thus confirming that the release of colloidal and supracolloidal material from sludge affects dewaterability, especially in the first days of digestion.

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